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INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part VIII. The Issue of Optimum Oxidant Control Strategy

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16. ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

Officials representing the states of Maryland, Wisconsin, Texas, Michigan, and New York reviewed the papers presented at the 1976 International Conference on Oxidants on the issue of optimum oxidant control strategy, and in Part VIII offered their viewpoints in regards to the current status and resolution of the issue and to the needs for additional research.

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Part VIII. The Issue of Optimum Oxidant Control Strategy

W. Bonta and J. Paisie
Department of Health and Mental Hygiene
State of Maryland
Baltimore, Maryland
Contract No. DA-7-1934A

P. Koziar and B. Becker
Department of Natural Resources
State of Wisconsin
Madison, Wisconsin
Contract No. DA-7-2175A

L. Jager
Department of Natural Resources
State of Michigan
Lansing, Michigan
Contract No. DA-7-2044A

G. Wolff
Interstate Sanitation Commission
(New York, New Jersey, and Connecticut)
New York, New York
Contract No. DA-7-2005H

F. Spuhler and K. Waid
Texas Air Control Board
State of Texas
Austin, Texas

Project Officer

Basil Dimitriades
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

Officials representing the states of Maryland, Wisconsin, Texas, Michigan, and New York reviewed papers presented at the 1976 International Conference on Photochemical Oxidant Pollution and Its Control concerning the issue of optimum oxidant control strategy and presented their views on the current status and resolution of the issue and on the needs for additional research.

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INTRODUCTION

Basil Dimitriades and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted out by EPA to scientists (who do not work for EPA or industry) with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of optimum oxidant control strategy. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow.

THE ISSUE OF OPTIMUM OXIDANT CONTROL STRATEGY

Basil Dimitriades and A. Paul Altshuller

As discussed in the introduction paragraphs preceding the first six issue sections, there are several questions or problems that must be resolved if oxidant control measures are to be developed and applied. Some of these questions, by virtue of their importance and basic nature, and the considerable contradictory attention paid to them, have attained an issue status and have been treated individually in the preceding sections. Resolution of those issues will definitely and considerably advance the understanding of the oxidant problem, but will still leave the primary issue of optimum oxidant control strategy somewhat open. There are still several questions more directly and specifically addressed to the subject of oxidant control strategy that need to be given definitive answers. These questions are to be dealt with in this section.

Departure points in this discussion/analysis will be two facts: The existence of an oxidant control strategy since 1971, and the generation, since 1971, of considerable new scientific evidence pertaining to the oxidant control problem. The immediate and obvious question that arises from these facts is whether the new evidence supports or invalidates, partly or wholly, the first, existing oxidant control strategy. If the strategy is shown to be invalidated in some respects, then the next obvious question is what strategy revisions are dictated or can be justified by the new evidence. To explore these questions or possibilities, it is necessary that the new scientific evidence, or, more directly, the changes in understanding brought about by the new evidence be specified.

The most important change in understanding that has been brought about by the new evidence concerns the source-receptor relationship, that is, the

geographical or spatial relationship between areas in which emissions are discharged and the areas where the air quality is impacted by these emissions. Much of the discussion needed here about this relationship has already been presented as part of the discussion on the Oxidant Transport issue. The control strategy implications, however, of the source-receptor relationships, as now understood, need to be further expanded.

The first implication is that long-range pollutant transport introduces a link between the urban oxidant problem and the rural oxidant problem. This means that in many areas, urban emissions and oxidant significantly affect rural air quality and, conversely, oxidant-carrying rural air upwind from a city significantly affects the city's air quality. Thus, from a control standpoint, the urban and rural problems are not entirely disassociated, and therefore, respective optimum control strategies should not be pursued entirely independent of each other.

A second implication is the one arising from the vertical mixing patterns observed and associated with radiation and subsidence inversion phenomena. Such mixing patterns suggest that local emissions may have significant carryover effects upon next day's local air quality. This and the previous implication depict a new picture of the photochemical processes responsible for a city's oxidant problem. According to this picture, the local oxidant problem is the composite of contributions originating from:

(a) local, fresh emissions,
(b) local but previous day's emissions,
(c) extraneous emissions (probably from previous days), and
(d) natural sources.

The third implication relates to the relative roles of the HC and NO_x emissions in the oxidant problem. The existing oxidant control strategy formally recognizes only a HC role; no oxidant-related controls are imposed upon NO_x emissions. Such roles of the precursors, however, are now thought to be incorrect quantitatively and, perhaps, qualitatively also. Thus, the oxidant-to-HC dependence is not independent of the NO_x factor. Also, and more

importantly, the effects of local HC and NO_x emission controls on oxidant are expected to vary depending on whether the oxidant results from local fresh emissions or from previous day's local emissions or from extraneous emissions.

In the light of these implications of the recent scientific findings, the specific questions that need to be answered here are as follows:

1. Is the qualitative basis of the existing oxidant control strategy still sound? That is, is hydrocarbon emission control an optimum approach to urban oxidant reduction?

Because of the link between the urban and the rural oxidant problems, the answer must be based on considerations of both types of problem. Consideration must also be given to the situation in which local emissions have multiday carryover effects upon local oxidant. Finally, consideration should be given to the relative importances of the anthropogenic and the natural sources. In essence then, the first question asked here can be reworded as follows:

> Considering the four origins of *urban* oxidant [cases (a) - (d) described in preceding paragraphs], is control of local (urban) HC emissions expected to be an effective means to local oxidant reduction?

Relevant evidence consisting of both laboratory and field data has been reported at the International Conference and elsewhere, and is conflicting. Thus some field studies showed HC control to have a strong beneficial effect, others did not show a detectable effect, and others showed effects varying with attendant NO_x emission change. Smog chamber studies showed that for the portion of oxidant formed from the day's local emissions, control of HC is beneficial except for atmospheres with extremely high — ordinarily not observed — hydrocarbon-to-NO_x ratios; for such atmospheres HC control, unless drastic, will have very little effect. For the portion of oxidant formed through multiday irradiation of emissions, the evidence is considered scant and inconclusive by some investigators but conclusive by others. Those who feel that the evidence is conclusive claim that HC control will have small effects upon multiday, irradiated air masses, relative to the effect upon single-day, irradiated air. Control of HC emissions upwind, again, has little

effect according to some investigators, undetermined effect by others. While it is certain that the effectiveness of the HC control approach is different for different localities, the judgment called for here is whether this approach should be retained or replaced by another approach.

2. Insofar as the urban oxidant problem is concerned, is NO_x emission control imperative? desirable? tolerable? undesirable? intolerable?

Again, for the questions to be answered properly, consideration must be given to the various sources of urban oxidant, namely, pollutant transport, local/fresh emissions, local/aged emissions, and natural sources. Evidence from field studies is conflicting in that it shows higher NO_x emission rates to be associated with lower oxidant concentrations in some cases, and no such association in others. Smog chamber data exist only for the situation in which the urban oxidant forms from the day's local emissions. For this situation, NO_x control has varying effects depending on the hydrocarbon-to-NO_x ratio of the reacting emissions. The effect of control of the upwind emissions of NO_x also may be in dispute. Again, as with the preceding question, the judgment called for here is whether the NO_x emission factor should continue to be nearly ignored — as is the case with the existing strategy — or should be considered, and how.

The preceding paragraphs dealt with the qualitative bases of an optimum oxidant control strategy, that is, with the questions pertaining to the directional impacts of the HC and NO_x emission controls. The questions that need to be defined next deal with the quantitative bases of an optimum strategy, that is, with the quantitative impacts of controls. Such quantitative bases consist of the following two components:

- The quantitative relationship between ambient oxidant concentrations and emission rates, and
- The definitive relationship between source area and receptor area, meaning the definition of the geographical area where the required control — *as calculated from the oxidant-emission relationship* — must be applied to solve the oxidant problem observed in a given locality.

The quantitative relationship between oxidant and emissions is the subject of the issue on the replacement of the Appendix-J method, and will not be treated here. Nevertheless, it might be helpful to mention here that the smog chamber method proposed as a replacement of the Appendix-J method provides a cause-effect relationship between oxidant and precursors, and unlike the Appendix-J method, does not take any specific source-receptor relationship for granted. Thus the smog chamber method does not prescribe, as the Appendix-J method does, that control be confined within the urban area where the oxidant problem was observed.

Assuming that the replacement of the Appendix-J method will be a method based on a cause-effect relationship between oxidant and emissions, it will be necessary that "cause" and "effect" be identified, respectively, with a "source area" and a corresponding "receptor area," the latter being the area where the air quality is impacted by the source area.

Defining the source-receptor relationship consistent with the cause-effect nature can be approached, in theory at least, in several different ways. By one, first approach, "effect" is identified with the maximum oxidant observed in the "receptor" area, and "cause" is identified with the emissions from *all* sources — *local and upwind* — that impact the receptor area. This approach requires that all source areas impacting the receptor area be identified, a requirement that is extremely difficult — if at all possible — to fulfill.

By the second approach, "effect" is identified with the fraction of the observed maximum oxidant concentration attributable to the local emissions, and "cause" is identified with the local emissions. This approach has at least two problems:

- The determination of the oxidant fraction associated with the local emissions, and
- The requirement that another source-receptor relationship be defined for the fraction of oxidant associated with the extraneous, upwind emissions.

The first problem is not an insolvable one; e.g., a rough estimate of the oxidant fractions associated with the local and the extraneous emissions could be obtained from oxidant measurements upwind and downwind from the receptor area. The second problem, however, is extremely difficult — if at all possible — to solve.

A third approach could be conceived as a simplified compromise between the two preceding ones. By this third approach, "effect" is identified with the maximum oxidant concentration observed in the receptor area, and "cause" is identified with the local emissions. The assumption is made here that the local emissions are the sole and whole cause of the oxidant problem. This assumption - it is well recognized - is not valid in oxidant transport situations in which the local emissions cause only part of the problem. Nevertheless, the assumption is justified on grounds that in the very same (oxidant transport) situations, the local emissions almost surely contribute to or cause additional problems to downwind areas. It might appear at first glance that application of controls calculated by this approach upon the receptor area as well as upon the upwind areas will result in over-control. In actuality, however, this will not necessarily be the case because the sum total of the "local" and "transported-in" contributions to oxidant may exceed the 0.08-ppm standard even though the individual contributions are each less than 0.08 ppm.

Finally, a fourth approach could be conceived as a more-stringent-control version of the second approach. By the fourth approach, "effect" is identified with the *fraction* of the maximum oxidant concentrations attributable to the local emissions. However, calculating control requirements so as to reduce a *fraction* of the oxidant down to 0.08 ppm, obviously, will not solve the oxidant problem. To solve the problem, control requirements should be calculated so as to reduce the "local" oxidant fraction below 0.08 ppm, that is, to a level such that the *total* oxidant will be, if possible, at or below 0.08 ppm. Thus, by the fourth approach, the oxidant contribution from the extraneous (upwind) sources is partly or wholly offset by imposing increased control of local emissions.

The preceding analysis identified four conceivable approaches to formulating an optimum strategy for oxidant control. Obviously, there may be others. The question to be asked here is:

> Which of these four, or any other approaches, is the one to be recommended?

REVIEW AND ANALYSIS

William K. Bonta and Joseph W. Paisie

INTRODUCTION

We find that answering the question on the "issue of the optimum oxidant control strategy" is considerably more difficult a chore than first anticipated. Our goal in Maryland has been to maintain a reasonable grasp of the state-of-the-art photochemistry and related modeling so that our oxidant abatement program is kept progressing on a relatively informed basis. Our program has for the most part consisted of following the Federal, new car program and the California stationary source control regulations. In contemplating the question, we ask ourselves if there were not abatement programs now in existence, where would we start? The answer becomes more difficult as our insight broadens.

Since the issue is whether or not to change that National strategy adopted previously, we first look toward the basis for existing policy. To do this from a state perspective is very difficult and we hope the following is not too inaccurate.

Although we were not directly involved in the original National policy development, it appears from references to the advisory panel and Congressional proceedings that some of these questions were discussed at that time. At any rate, the policy adopted in 1967, merely 10 years ago, was to control hydrocarbons only. Again, though we were in a peripheral position in 1970, it is our understanding that the control of NO_x was added to the program by the Congress for the sake of the NO_x impacts alone and not because of the influence on photochemical oxidant production.

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We feel fairly confident that the present EPA oxidant control strategy was based upon three premises contained in the photochemical oxidant criteria document (2). The first premise was that photochemical oxidants were only an urban air pollution problem. The second premise was that, in urban atmospheres, there were very large emissions of both organics and oxides of nitrogen. The available evidence from smog chambers indicated that the optimum photochemical oxidant control approach in such a situation would be to control organic emissions. The final premise was the presumption that the local photochemical oxidant levels were the result of local precursor emissions. The role of rural precursors was thought to have little impact on the urban situation; the levels of oxidant measured in rural areas at that time were less than 0.07 ppm. Any ozone transported to the urban areas was thought to react with morning NO emissions in the suburban fringes, and thus, the zero background assumption was thought to be justified.

The mechanistic picture of the photochemical oxidant problem has been altered as a result of EPA studies (3-7) which discovered rural oxidant levels 2 to 3 times the national ambient standard. These discoveries have changed this early concept in several ways. First, the literature has suggested that oxidant and/or precursors can be transported in significant quantities from urban areas to rural areas and vice versa. The implication is that the closed system (smog chamber) may not accurately simulate all situations of elevated oxidant as the early premise assumed. Secondly, the problem of photochemical oxidants has been demonstrated to be more widespread than originally thought and definitely not restricted to urban areas. Finally, the roles of hydrocarbons and oxides of nitrogen may be different than perceived earlier; i.e., hydrocarbon may not always be the limiting reactant as was assumed earlier. This especially applies to rural areas.

The impact of this new information is one of raising questions concerning the current EPA control strategy. This review will consider the recent information concerning the state-of-the-art oxidant control strategy and recommend changes based on this new information.

QUALITATIVE ASSESSMENT OF CURRENT CONTROL STRATEGY

The fundamental chemistry between organics and oxides of nitrogen in a photochemical atmosphere must be defined in a closed system. This requirement dictates the use of a smog chamber. The results of these experiments (Dimitriades (8), Jeffries et al. (9) and others) has identified this fundamental qualitative relationship for the lower concentrations typical of urban atmospheres. Quantitatively, the results have not agreed as well. However, it is unarguable to say that these experimental results have not been contradicted. The results of these experiments have been extended by Dodge (10) through the use of chemical kinetic models to conditions which were not experimentally practicable, i.e., very high and very low ratios of nonmethane hydrocarbons to oxides of nitrogen, i.e., greater than 12/1 and less than 2/1. Certainly, there is a degree of risk involved in extrapolating into these areas through the use of a model; however, the results of this extrapolation seem reasonable and are usable. Therefore, the results of these experiments determine the basic role of organics and oxides of nitrogen in the photochemical oxidant generation process. Qualitatively, these results do not differ from the earlier results produced in smog chambers (11). Therefore, the fundamental roles of organics and oxides of nitrogen have not changed.

The change that has prompted a reevaluation of the oxidant control program is the perception of the meteorological phenomena affecting the production of photochemical oxidants. The early smog chamber work was an adequate simulation of a "first day" urban situation, i.e., the situation in which fresh urban emissions are released into a relatively clean atmosphere. It is our opinion that this is an overly simplistic picture of the urban situation. The urban problem is the result of many factors influencing the production of oxidants. Included in these phenomena are elevated stable layers of ozone and precursors which may be the result of the urban area itself or transport from other areas. Other factors are the effects of natural phenomena such as the stratospheric intrusion of natural ozone and natural precursor emissions. The evaluation of the control strategy in urban areas is complicated by these factors.

The paper by Sickles et al. (12) demonstrates that relatively small amounts of precursor, which are the leftover products of a first day irradiation, can generate significant amounts of ozone. These results support the diffusion modeling analysis of Dabberdt and Singh (13). These authors modeled stringent control strategies which reduced both organic emissions and oxides of nitrogen and were initiated after 2 or 3 days of an episode situation. The results indicated that a very small reduction in ambient oxidant levels could be expected as a result of the control strategies. Certainly, the quantitative conclusions drawn by this modeling analysis may be erroneous since the reliability of the results of photochemical diffusion models is questionable at this time. However, the qualitative results of this analysis appear to be correct. These results may be further supported by the work of Cleveland et al. (14), which demonstrates that Sunday levels of oxidants, with reduced emissions of both organic and oxides of nitrogen emissions, do not necessarily result in a corresponding decrease in photochemical oxidant level. It is our opinion that these results demonstrate that when considering a short-term situation, the effect of organic and oxides of nitrogen reduction may not result in a concomitant reduction in oxidant concentrations.

The long-term analysis of this situation indicates somewhat different results. The use of trend analysis is very helpful in the evaluation of the long-term effects of the EPA control strategy. The work of Trijonis et al. (15), in considering the trends in oxidant and precursor trends in an urban area (Los Angeles), is very helpful. This work indicates that the basinwide emission trend of organics is down by 18% and the emission of oxides of nitrogen is up by 36%, resulting in a basinwide reduction in oxidant of 19%. These results correspond qualitatively with the prediction that would be made using the smog-chamber diagram and a ratio of nonmethane hydrocarbons to oxides of nitrogen that would be appropriate to an urban area. Therefore, the qualitative behavior of the Los Angeles atmosphere is expected. This study cannot by itself demonstrate the quantitative relationships between the dependent and the two independent variables.

The study by Trijonis et al. is further supported by the study of Martinez et al. (16). The analysis performed in this study, which was mainly concerned

with San Francisco, demonstrates that oxidant reduction in the Bay Area was correlated with organic emission reduction. However, the correlation between the NMHC/NO_x ratio and the oxidant reduction is more significant. Again, this is an expected result considering the existing model for the behavior of a "typical" urban atmosphere; i.e., reducing levels of organics and raising levels of oxides of nitrogen will result in lower levels of oxidant. We hesitate to use the term "typical" here because of the obvious differences between the California basin situation and those of other U. S. cities.

The final report relating the behavior of photochemical oxidants with EPA control strategy of organic emission reduction was conducted by Altshuller (17). This study, which was conducted using the CAMP station data in six urban areas, demonstrates a reduction in oxidant levels. It was shown that the trend in emissions in these metropolitan areas is similar to that found in Los Angeles and San Francisco, i.e., a reduction in oxidant concurrent with a reduction in nonmethane hydrocarbon levels. The study showed that oxides of nitrogen levels did not increase in three of the data sets. Whether this observation eliminates our concern over the relative split between the effects of the precursor changes (that is, that oxidant reduction occurs with hydrocarbon reduction while keeping NO_x constant) may be an anomaly generated by large gaps in the NO_x data.

The general body of observational evidence indicates that, qualitatively, the role of organic emissions in the formation of urban oxidants has not changed in the past years. This conclusion is based only on the results of analysis of urban situations. The trend information has indicated that, in spite of elevated ozone layers, carryover of oxidant and precursor, and natural sources of precursor, urban oxidant levels have decreased. The major problem with these analyses is that for most of the urban areas under consideration, it is difficult to separate the effect of the decrease in organic emissions from an increase in oxides of nitrogen emissions. We conclude that is not possible to attribute the reduction in urban oxidant levels to reduction in organic emissions alone.

The role of organic precursor emissions in the production of rural oxidants is not as clear as the urban situation. The available information indicates that a number of processes are available that could conceivably contribute to levels of rural oxidant. Among the processes are the transport of mature ozone from urban areas, multiday irradiation of transported urban precursor, stratospheric intrusion of ozone, irradiation of natural precursors, irradiation of transported urban precursors, and irradiation of both transported urban precursors and fresh rural emissions. Each of these factors could contribute to the formation of rural ozone. The available information does not indicate what quantitative relationships are applicable. In addition to this, the NMHC/NO_x ratio in rural areas is considerably higher than the corresponding ratio in urban areas. With this increase in ratio, the relationship between organic precursor emission and resulting oxidant may change. According to the extrapolated smog chamber diagrams, which we believe represents the chemistry of the rural atmosphere, at high ratios (>30/1) of NMHC/NO_x, the level of resultant oxidant does not appear to be significantly related to the level of organics; i.e., reduction of organics will not have an effect on oxidant levels until great reductions on organic levels are achieved. The information presented at the International Conference which would present real world confirmation of the rural generation theorum is somewhat confusing.

The paper presented by Hathorn and Walker (18) attributes the primary source of rural ozone to stratospheric intrusion of ozone-rich air. The hypothesis that stratospheric intrusion does occur has been advanced by others (19) and the phenomenon is sufficiently well documented to accept its occurrence at least occasionally. However, the data presented by Hathorn and Walker does not conclusively demonstrate their case. Tracer information, which could demonstrate where the ozone originated, was not presented. This makes interpretation of the data very difficult. Additionally, the lack of supporting data, both meteorological and chemical, makes the case very weak. They do not quantify the fraction of ozone due to stratospheric intrusion. We are of the opinion that attributing stratospheric intrusion of ozone as the primary rural source is a "leap of faith" that is not supportable using this data. The hypothesis is interesting, however, and we wonder if a sophisticated statistical analysis would not disprove the theory.

Another potential source of rural ozone is transported urban ozone and precursor. The work of Sickles et al. (12) utilizing smog chamber simulation of rural atmospheres is useful in demonstrating this phenomenon. This work demonstrates the effects of dilution and second and third day irradiation of urban atmospheres on the production of photochemical oxidants. The experimental data demonstrates that the "dilution effect" occurs and can be a major contributor to rural ozone. However, the half-life calculations indicate that previous day's ozone can exist for only 20-30 hours. This implies that high rural oxidant levels lasting for more than 2 days could not occur if it were only the result of re-irradiation of diluted urban air masses. It follows that fresh precursor emissions are necessary to the process, if continuing high levels of rural ozone are expected to occur. The question of which precursor is necessary to the process is not clear. The critical parameter to be considered is the NMHC/NO_x ratio. If this ratio is greater than 75/1, using the data of Sickles et al. (12), the effect of additional organics is not important and NO_x becomes the crucial factor. If the ratio of NMHC/NO_x is less than 75/1, the crucial factor is the effect of additional organics. This information indicates that rural oxidant can be the result of transported urban precursor and oxidant plus fresh precursor from the rural areas. Which precursor is necessary would depend on the NMHC/NO_x ratio. The problem with this analysis is that no quantification is presented concerning the impact of urban precursor and oxidant or rural oxidant.

A third body of information concerning the origin of rural oxidant is the study of Meyer et al. (20). The use of trajectory analysis, as was done in the study, is useful in determining the relationship between meteorological and emissions parameters and resulting levels of photochemical oxidants. The process used is probably not quantitatively useful because of inaccuracies in input data. The results indicate that meteorological parameters are more highly correlated with oxidant levels than emission characteristics. This is consistent with other studies. This study demonstrates that both upwind and local emissions of organics are positively correlated with observed levels of photochemical oxidants in rural areas. An interesting result, however, is the positive correlation of NO_x emissions of the previous day.

Based upon all the information, the role of organic emissions in rural oxidants is dependent upon the NMHC/NO_x ratio. Smog chamber diagrams indicate that at sufficiently high NMHC/NO_x ratios (>30/1) the effect of organic emission control or oxidant production diminishes. There is a hint that atmospheres of this sort may exist in Meyer's trajectory analysis. The problem is that at the present time not enough monitoring data is available to determine where areas with a ratio greater than this occur, if they occur at all. Until such time as more data is available and the proper analyses can be made, it is not possible to determine those areas where it is certain that organic emission control in rural areas is beneficial. In addition to this, the impact of natural emissions of organics, which may produce significant rural oxidants at ratios of approximately 15/1 and 25/1, has not been assessed. The entire rural situation needs greater study and a more complete quantification before a definitive answer concerning the effect of organic emission control can be formulated.

Based upon the above discussion, we are of the opinion that the role of organic precursors in rural atmospheres is not clear. The determination of the role of organics must be based upon an adequate knowledge of the spatial distribution of NMHC/NO_x ratio in rural areas. The information available is insufficient to adequately address this question.

The next important topic in this assessment of the current oxidant control strategy concerns the role of oxides of nitrogen. The current strategy does not recognize the role of NO_x in the production of photochemical oxidants. The recent information presented at the International Conference on Photochemical Oxidant Pollution and Its Control may require that this judgment be reconsidered.

The first task in the reconsideration of the role of oxides of nitrogen in the photochemical oxidant production process involves a discussion of the urban situation. Again, it is necessary to rely on the work done in somg chambers (8,9) to determine the qualitative chemical relationship between oxides of nitrogen and photochemical oxidant production. The work that has been done using concentrations of organics and oxides of nitrogen that can be

considered typical of our urban atmosphere and a correspondingly typical ratio of NMHC/NO_x has demonstrated that increasing NO_x, at constant organic concentration, results in reduced levels of oxidants. The oxide of nitrogen added is NO, a well known scavenger of ozone. This phenomenon has been noted many times, especially in the placing of air monitoring stations near heavily traveled roads.

Ambient studies on the effects of changes in concentration of oxides of nitrogen on urban oxidants have demonstrated this behavior. The work of Trijonis et al. (15) in Los Angeles, discussed earlier, demonstrated that increasing concentrations of NO_x and decreasing concentrations of organics has resulted in a reduction in oxidant. This qualitatively agrees with the predictions of smog chamber. However, the work does not demonstrate the quantitative relationship involved.

The work of Martinez et al. (16) has also demonstrated that urban levels of oxidant are most sensitive to the NMHC/NO_x ratio. Specifically, the work has shown that decreasing the NMHC/NO_x ratio, which can be accomplished by reducing NMHC at constant NO_x or increasing NO_x at constant NMHC is related to decreasing levels of photochemical oxidants. This evidence is a further indication that the qualitative predictions of the smog chamber are substantiated in an urban atmosphere.

The only ambient study that would, at face value, tend to contradict these results is the study of Van Ham and Niebor (21). This study shows that addition of NO_x to an air sample results in increasing photochemical oxidant production. This is a difficult study to interpret since a complete NMHC/NO_x ratio is not reported. If the ratio had been reported, it would be possible to assess more adequately the results. If the ratio of NMHC/NO_x were sufficiently high, i.e., a system that is NO_x deficient, the addition of NO_x would increase oxidant production. If the sample were organic deficient, i.e., a low NMHC/NO_x ratio, the results of this study would be contrary to the results of other investigators and a more in-depth analysis of the procedures and the results would be necessary. Without the NMHC/NO_x ratio, the study

must be considered inconclusive. A repetition of the study with a more complete data set would be in order.

Based upon these data and results, the control of oxides of nitrogen in urban areas to control urban oxidant is unnecessary and would be counter-productive. However, before reaching a final judgment on the control of oxides of nitrogen, one must consider the rural area problem where the role of NO_x is not as clear.

Ambient monitoring in rural atmospheres (3-7) indicates that, in general, rural atmospheres are characterized by high NMHC/NO_x ratios and levels of NO_x that are at or near the minimum detectable limit of the instrument, i.e., 0.005 ppm for an hour. The NO_x present in rural atmospheres is almost totally NO_2, which is an ozone precursor (as opposed to NO, which is an ozone scavenger). Therefore, the effect of additional NO_x in rural atmospheres would depend upon which form of NO_x is added to the rural atmosphere and where the effect is to be measured. If a rural source of NO_x is to be considered, the emission from fuel burning will be mostly NO. Therefore, in the neighborhood of the source, one could expect a decrease in ozone because of the NO-ozone scavenging reaction. However, farther away from the source, one could expect that the NO will be converted to NO_2, and the concentration of NO_2 will be decreased by dilution. This could result in an increase in oxidant production. Similarly, one could expect that increased NO_x emissions in urban areas could be transported to rural areas as NO_2. The increase in urban NO_x emissions could be expected to expand the region of the rural area affected by urban oxidant and precursors.

This picture of the rural oxidant situation is supported by the work of Meyer et al. (20). While the trajectory analysis approach used in the study has many limitations and only 40% of the observed variance is explained by the correlations performed, the qualitative picture of rural oxidant delineated in the study is similar to that described previously. The major finding in this study with respect to NO_x may be the confirmation in situations other than the California basins that NO is probably a scavenger of ozone and NO_2 may be an ozone generator. The results indicate that the

previous day's emissions of oxides of nitrogen were positively correlated with observed levels of photochemical oxidant. Emissions of NO_x on the day the oxidant is observed are negatively correlated with levels of ozone.

Another study concerning the role of oxides of nitrogen in the rural atmosphere is that of Sickles et al. (12). This study demonstrates the effect of changes in NMHC/NO_x ratio on ozone maxima and ozone generation. This study has determined that a maximum occurs in the relationship between the NMHC/NO_x ratio and the amount of ozone generated. This maximum occurs at NMHC/NO_x ratios equal to approximately 75/1. At ratios lower than 75/1, decreasing the ratio decreases ozone. At ratios greater than this, decreasing the ratio will result in increased ozone production. These results are qualitatively consistent with other smog chamber experiments (8,9) relating the effect of the NMHC/NO_x ratio on ozone production. However, the critical ratio in these studies ranges from 15/1 to 30/1. The important fact is that this phenomenon has been demonstrated.

The foregoing qualitative discussion of the current EPA control strategy has addressed the role of the precursor pollutants in a segmented fashion; i.e., it has discussed the urban situations separate from the rural situation and has discussed the role or organic emission control separate from oxides of nitrogen control. This is not the proper way to analyze photochemical oxidants. The EPA studies concerning transport have clearly demonstrated that the urban problem and the rural problem are not inseparable. Therefore, a discussion of the coordination between urban and rural phenomena is necessary. To discuss this aspect of the current control strategy, it is necessary to first outline a few more observations.

The current EPA control strategy with respect to automobile emissions has been aimed at the two types of automotive emissions, i.e., exhaust and evaporative. The trend in automobile emissions from Black's (22) study shows lower mass amounts of emissions as well as a change in composition. It also shows that evaporative emissions are becoming larger than exhaust emissions. The addition of catalysts has effected a change in composition of exhaust emis-

sions with the trend toward a greater percent of paraffinics. Additionally, the composition of evaporative emissions from automobiles is mostly paraffinic with n-butane and isopentane being the dominant constituents.

The trend in stationary source emission control is outlined by Walsh (23). Basically, the past strategy for stationary sources was based on Los Angeles' Rule 66 controls. This strategy was based upon reactivity and substitution of slower reacting solvents for rapid reacting solvents. This strategy resulted in solvent reformulation and substitution. However, it did not result in a great reduction in the tonnage of emissions from stationary sources. The future strategy will be based on positive organic emission control.

The present control program for oxides of nitrogen relies on the control of automotive emissions. The new-car control program is the only aggressive program for control of this pollutant presently in force. Stationary source NO_x control has not been initiated except in California. With these observations in mind, the next step is to evaluate the impact these existing strategies will have on ambient levels of oxidant.

Obviously, the present strategy will reduce levels of organic compounds in urban or source areas. This, coupled with the fact that the automobile control program, specifically the catalytic converter, will result in emissions of organic compounds requiring longer irradiation to reach maximum oxidant concentrations, will result in lower levels of ozone. This will be aided by the fact that oxides of nitrogen emission controls have been delayed. Consequently, it can be expected that the urban ratio of $NMHC/NO_x$ will continue to decrease and will result in lower urban oxidant levels. The result of this action in the urban areas may be an increasing carryover of urban emissions into rural areas. This will definitely be true for oxides of nitrogen and may be true for organic emissions. This can be expected to deliver more precursor to rural areas where further irradiation can generate oxidant. Indications from the study of Sickles et al. (12) are that urban oxidant cannot last more than 20-30 hours in a rural area, based upon half-life measurements both in the chamber and in the ambient atmosphere. There-

fore, since generation of oxidant is already occurring in rural areas, the expanded carryover of urban precursor into rural areas can be expected to accelerate this process. Additionally, reduction in urban organic precursor without a concomitant reduction, or at least holding of the line, in emissions of urban oxides of nitrogen could result in an expansion of the current rural oxidant problem since most rural atmospheres appear to be NO_x deficient. Thus it appears that positive control of urban organic emissions is necessary and must be continued. Control of urban oxides of nitrogen emissions is necessary for the benefit of rural areas. However, the control of urban oxides of nitrogen is counterproductive when considering urban oxidant. Therefore, the best policy for the interim is to maintain urban oxides of nitrogen at their current level. If abatement of oxides of nitrogen is to be initiated in urban areas, the control of organic emissions must be coordinated with this program to ensure that the $NMHC/NO_x$ ratio continues to decrease.

The precursor control program in rural areas is not as clear. The atmospheric levels of organics and oxides of nitrogen in rural areas have not been adequately defined. Therefore, any recommendations for rural areas must necessarily be speculative. However, it can generally be said that rural atmospheres would probably tend to be NO_x poor. The ratios of $NMHC/NO_x$ can be expected to be high relative to the urban area. The question is how much higher. If rural atmospheres have ratios greater than 75/1, as per Sickles et al. (12), the control of oxides of nitrogen appears to be the best method for control. If ratios are less than this, organic emission control can be expected to be effective. Until more data is available, this is pure speculation.

SOURCE-RECEPTOR RELATIONSHIP FOR OXIDANT CONTROL STRATEGIES

The preceding section dealt with the fundamental chemical relationship between oxidant precursor and oxidant. This section will deal with the consequences of meteorological transport on the oxidant production process and how it bears on the source-receptor relationship in photochemical oxidant control strategies.

The current EPA control strategy is based upon the following source-receptor relationship. Precursor concentrations of organic compounds in the 6-9 a.m. time period at a given location are associated with the photochemical oxidant concentrations measured near that location later in the same day. This view of the oxidant production process has been seriously questioned as a result of the EPA transport studies and measured levels of rural oxidants. We feel that this concept of the oxidant production process is incorrect and must be modified. A number of alternatives have been suggested. Each of the alternatives attempts to define the correct source-receptor relationship, i.e., a cause-effect relation.

The first alternative identifies the effect with the maximum oxidant observed in the "receptor" area. The cause is associated with all sources both local and upwind. This approach is the most complicated approach to be suggested since it requires that a complete tropospheric ozone budget be developed for every urban area experiencing oxidant levels elevated above the standard. This type of information is not currently available since many factors in the tropospheric ozone generation process are still inadequately quantified, e.g., natural emissions, stratospheric ozone intrusion, and natural scavenging mechanisms. Therefore, this approach, which may be the most realistic characterization of the source-receptor relationship, must be relegated to the distant future since it is simply too complex to be useful at the present time. As more data becomes available and the understanding of all the factors affecting tropospheric ozone is improved, this technique should be reconsidered.

The second alternative approach is to identify the fraction of observed maximum oxidant concentration attributable to the local emissions assuming that the local emissions cause this oxidant. Certainly, this method would allocate control properly, i.e., local sources would only be required to control in order to reduce the local contribution. The first problem with this approach would be the quantification of the contribution that local sources made to the local problem. This would require the use of a deterministic model which is not available for many areas in the country. The notable exceptions would be Los Angeles, San Francisco, Denver, and St. Louis. We

believe that, at this time, no other cities in the country have the necessary instrumentation or the clearly defined airshed in which one could perform this task. Application of this method to other cities in the United States is not insurmountable; however, it would require time and more resources than will likely be available in the near future. The second problem involves the determination of the source of the extraneous oxidant entering an urban area. This is the most difficult problem to solve. The transport studies of EPA show high levels of ozone associated with the back edges of high pressure systems. It would seem that these air parcels can have residence times as long as 4 days. Therefore, it seems highly unlikely that one can specifically identify the source of emissions that contributes to those elevated oxidant levels. This approach, therefore, is also too complicated to be used at this time. The combined need of a deterministic, quantitative oxidant model and a complete knowledge of the meteorological transport patterns occurring over synoptic scale areas of the United States makes this approach unworkable.

The third approach to be considered is based upon the concept that maximum oxidant observed locally is the result of only locally produced emissions of precursors. This assumption is not correct since it is well known that local emissions are not the sole cause of local maximum oxidant. However, it is known that the local emissions can be transported and affect a different receptor area at a later time. Therefore, this approach is one of requiring that each source area be concerned with its own problem and ignore the contributions from other areas. The major problem involved in this approach is that the possibility exists that over-control of local sources could result. Whether or not this will actually occur is a moot point at the present time since the type of information necessary to confirm or deny this is not available at the present time. Specifically, the complex qualitative relationship of transported and locally generated oxidant is not available at the present. However, from an administrative viewpoint, this approach is probably the most acceptable alternative. Each urban source area would be concerned with reducing its own emissions. EPA would have the responsibility to ensure that each urban area do the most to reduce its own level of emissions to ensure that the standard is not violated as a result of local emissions. This is a fairly conservative approach that could be justified as

being a reasonable method that allows states to develop their own implementation plans and keeps the EPA role to one of surveying the plans developed. In addition to this, the current data available in most urban areas would be sufficient to support this approach.

The final approach is similar to approach number two in that a fraction of local maximum oxidant concentrations is associated with local emissions. However, when calculating control requirements, the local fraction of the maximum oxidant is reduced to the extent that the national standard of 0.08 ppm is not exceeded. This means that the contributions from upwind sources is completely balanced by increased reductions by local sources. This approach requires that an agency know the contribution of local sources to the maximum oxidant concentration. This also requires a deterministic quantification of the local contribution to maximum oxidant; this is still a considerable problem. Additionally, it assumes that transported oxidant can never be greater than the standard. This may or may not be the case. Washington, D. C., and Baltimore are two large metropolitan areas separated by only 40 miles. The possibility of transport of large amounts of ozone between these two metropolitan areas is quite likely. Therefore, Baltimore may never be able to control sufficiently to attain the standard. A policy would need to be developed relative to this situation since it may be repeated many times on the east coast. Finally, the possibility of over-control exists under this approach. As upwind sources reduce their contribution to an urban area, the need for the restrictive controls on local sources will diminish.

Based upon the foregoing discussions, the third approach appears to be the most amenable to usage in controlling photochemical oxidant. The other approaches may be more scientifically accurate, but they are not usable with the data base presently available in most urban areas. Certainly, as more data becomes available, reconsideration of the source-receptor relationship will be necessary.

CONCLUSION AND RECOMMENDATIONS

Based upon the above discussion, there are four recommendations we would like to make concerning the issue of the optimum oxidant control strategy. The first two recommendations concern the existing control program. The other two recommendations concern further work that could be done to improve the oxidant control program.

The first recommendation concerns the definition of the optimum oxidant control strategy. In the urban areas, positive control of organic emissions is necessary and must be continued. Control of urban emissions of oxides of nitrogen is necessary for the benefit of the rural areas. However, the control of urban oxides of nitrogen is counterproductive when considering urban oxidant. Therefore, the best policy for the interim is to maintain urban oxides of nitrogen at their current level. If abatement of oxides of nitrogen is to be initiated in urban areas, the control program must be coordinated with the organic emission control program to ensure that the NMHC/NO_x ratio continues to decrease. In the rural areas, the precursor control program is not as clear. Sufficient data is not presently available to adequately assess the problem. Therefore, any control strategy for reducing rural precursor for the benefit of rural area oxidant would be very speculative. Until more information is available, the control program for rural precursors should be held in abeyance.

The second recommendation concerns the source-receptor relationship for use in oxidant control programs. The approach that is most usable at the present time is based upon the assumption that urban area emissions are solely responsible for the observed oxidant maximum in that urban area. This is a simplification of more complex precursor-oxidant relationships which are more scientifically valid but are too complicated to be of value at the present time. The available data would support the use of this method. This technique should be viewed as an interim approach that can be changed as the more valid relationships become usable.

The third recommendation concerns the consolidation of all the information relating to the phenomenon of photochemical oxidant pollution. Specifically, work needs to be done to compile a quantitative model of photochemical oxidant pollution. This model should include urban-rural interactions, the role of natural precursor, and the role of stratospheric intrusion. At the present time, these phenomena have been considered in piecemeal fashion in the literature. Work needs to be done to integrate all the current information into a comprehensive quantitative assessment of photochemical oxidant pollution. Without this type of work, control strategy development will remain speculative and qualitative. We believe this is an enormous task; however, as the process is initiated, it will crystallize the available knowledge and will enphasize those aspects of the problem that need further research.

Finally, as pointed out earlier to EPA (24), we are of the opinion that there is a need for a different administrative mechanism for coordinating whatever multistate abatement strategies are adopted. Though there is provision in existing law that the states must provide in the SIP for interstate coordination of the abatement programs, our own observations have demonstrated that such an indirect approach has been somewhat ineffective applied to the traditional pollutants in the past. When the same argument is applied to photochemical oxidants in an area that may be comprised of several EPA Regions, it is clear to us that the current governmental machinery needs work. Whether or not new amendments to the Act must be proposed remains to be seen. Perhaps an interpretive ruling on the regulations that require this interstate mechanism will get the necessary attention to the matter. We feel assured that this type of problem will be similar for the sulfate problem that EPA may be facing shortly.

REVIEW AND ANALYSIS

Paul Koziar and Brooks Becker

SUMMARY

At the request of the United States Environmental Protection Agency a review of the recent scientific literature pertaining to the photochemical oxidant problem was conducted. The literature reviewed was obtained from technical journals and from papers presented at the International Conference on Photochemical Oxidant Pollution and Its Control and at the Specialty Conference on Ozone/Oxidant Interactions with the Total Environment. This review was prepared to evaluate the qualitative basis for the existing oxidant control strategy and to recommend an optimum urban oxidant control strategy identifying the direction that hydrocarbon and nitrogen oxide control should take.

The four quantitative approaches for an optimum urban oxidant strategy suggested by EPA were reviewed in order to recommend one or to suggest alternatives.

Field and lab data were reviewed both independently and compared with one another to evaluate the scientific evidence presented. After studying the evidence, it is our opinion that the control of hydrocarbon emissions is the optimum urban oxidant control strategy.

On the basis of scientific evidence, the control of nitrogen oxides is judged to be tolerable, but from the implementation standpoint, it is undesirable at this time.

Of the four quantitative control approaches suggested, the one judged best is Approach IV. This approach utilizes the fraction of the maximum oxidant concentration as a means of determining local control but implies that further local control may be necessary to offset extraneous emissions. Although Approach IV is the best of those reviewed, modifications to it are suggested, and these are described in the section on Quantitative Evaluation, the Comparison of Approaches subsection.

DIRECTIONAL IMPACTS OF CONTROL — QUALITATIVE EVALUATION

Natural Source of Oxidants

Natural ozone occurs in the troposphere as a result of both meteorological phenomena and the photooxidation of natural emissions of hydrocarbons and nitrogen oxides. The degree to which each of these mechanisms contributes to ozone concentrations at the ground level will be discussed below.

Ozone formed in the stratosphere may be transported to the lower layers of the troposphere in situations involving strong vertical mixing. Meteorological phenomena which may produce strong vertical mixing are:

- Active upper-level weather systems
- Intense squall lines ahead of cold fronts
- Large thunderstorm cells.

The first two meteorological conditions are usually associated with the same mesoscale weather system, whereas thunderstorms may occur independently as a result of local convective activity. The injection of ozone into the troposphere from upper-level low pressure systems or intense squall lines occurs as the tropopause (stratosphere-troposphere boundary) is brought closer to the earth's surface, thereby facilitating mass exchange of the stratosphere and the troposphere.

Large thunderstorms also may penetrate the tropopause and transport ozone to the surface in strong downdrafts.

Stratospheric transport of ozone, associated with active upper-level weather systems, has been investigated by numerous people. Using ozonesonde data gathered by the Air Force in the 1960's, Carney (25) concluded that most high tropospheric ozone (O_3) concentrations are the result of stratospheric transport. Sticksel (26), using the same data, estimated that mean monthly averages of ozone in the lower layers of the troposphere may be as high as 0.065 ppm, and daily concentrations may be as high as 0.12 ppm. A reexamination of this data by Chatfield and Harrison (27) indicated that ozone may range from 0.026 to 0.072 ppm in the middle troposphere. Chatfield and Rasmussen (28), using aircraft data, concluded that ozone ranges from 55 to 60 ppb across the United States, above the mixing layer.

The results of a study of ozonesonde data by Bach (29), which was gathered by the U.S. Environmental Protection Agency (30), indicates that stratospheric transport of ozone into the upper troposphere occurs, but changes in ozone concentrations below 3 km are primarily controlled by processes existing below the boundary layer. He also concluded that mid- to upper-tropospheric ozone can change by 50 percent during the day, but that these observed changes do not exert any direct control upon ground-level ozone concentrations.

Surface ozone measurements have also been used to estimate the impact of stratospheric ozone. Hathorn and Walker (18) analyzed surface ozone data during a widespread episode, and attributed high ground-level ozone to stratospheric transport of ozone. Chatfield ad Harrison (27) concluded that surface ozone from stratospheric transport ranges from 0.040 to 0.055 ppm. Their conclusions were reached from analyzing ground-based ozone data recorded in the northwest corner of Washington. An analysis of surface ozone data recorded in a remote area of western Colorado by Jones and LaHue (31) shows that hourly averages of ozone approached 0.08 ppm, but no one mechanism is suggested as the source.

Another meteorological phenomenon that has been suggested as a possible mechanism for stratospheric transport of ozone in the troposphere is vertical mixing associated with squall lines and thunderstorms. Davis and Jensen (32) conducted a comprehensive analysis of the effect of weather systems on low-

level ozone concentrations. They concluded that most ozone concentration rises, which occurred in association with squall lines on thunderstorms, were of short duration.

The photooxidation of natural emissions of hydrocarbons and nitrogen oxides also can contribute to ozone in the troposphere. Earlier studies by Rasmussen (33) indicated that the rates of organic emissions from vegetation, in the form of terpene-type compounds, are higher than from man-made emissions when compared on a global basis. Although the rate of organic emissions is high, Robinson and Rasmussen (34) further reported that the photochemical processes associated with natural emissions of hydrocarbons (HC) or nitrogen oxides (NO_x) account for about 0.02 ppm ozone. Their estimates were based upon the irradiation of rural air in Tedlar bags.

Gay and Arnts (35) also investigated the potential for oxidant formation from naturally emitted hydrocarbons. Measurements of natural hydrocarbon concentrations were made in and above a forest canopy. Concentrations of terpenes in the canopy were highest in the nighttime hours, but above the canopy, concentrations were very low. Irradiation of these terpene-type compounds yielded the following results:

- Terpenes react rapidly when irradiated with UV in the presence of NO_x.
- The ozone produced by irradiation is a function of the HC/NO_x ratio.
- Ozone reacts rapidly with terpenes.
- In rural areas, terpenes participate in aerosol formation, but the significance of their oxidant formation is low.

The scientific data in the recent literature presents conflicting evidence on the fraction of oxidants contributed from natural processes, especially the evidence presented for stratospheric transport of ozone to the surface layers. Although most investigators agree that the contributions from natural sources of oxidants exist, they disagree on the magnitude of the contribution.

Based upon our judgment of the conflicting evidence regarding the contribution of natural ozone sources to the surface tropospheric ozone budget, we have reached the following conclusions:

- Stratospheric transport of ozone is significant and may be the prime contributor to exceeding the ozone standard (0.08 ppm) in some cases.
- Ozone contributed from stratospheric transport alone cannot explain the frequency and duration of oxidant concentrations exceeding the standards or the maximum oxidants recorded at urban sites.
- The overall contribution of ozone from natural hydrocarbon emissions alone is judged to be generally smaller than that of the stratosphere, but may be higher in areas where specific combinations of plant communities emitting terpenes exist.
- In geographic areas where the additive effect of ozone from the stratosphere and photooxidation of natural emissions can occur, the frequency of exceeding the NAAQS is greater than from the individual sources alone.
- Ozone contributed from both stratospheric transport and natural emissions cannot explain the frequency and duration of oxidants exceeding the standards or the maximum oxidants recorded at urban sites.

The conclusions reached here regarding the contribution of natural emissions have some anthropogenic precursor control implications:

- That precursor emissions from anthropogenic sources are the prime contributors of *maximum* oxidant concentrations recorded at the surface.
- That the control of anthropogenic precursors is necessary to reduce oxidant concentrations in urban areas.
- That the extent to which the control of precursor emissions can attain the standards is dependent upon the localized influence of natural emissions.

Anthropogenic Sources of Oxidants

In the previous section, natural sources of oxidants were discussed to evaluate their contribution to the control of photochemical oxidants. To

evaluate the effect and required control of anthropogenic precursor emissions, relationships between the *source* of precursor emissions and the maximum oxidants recorded at the *receptor* must be quantified.

Prior to 1970, the relationships of oxidants to hydrocarbons and nitrogen oxides were derived from data recorded only in large urban areas (2). Recently though, monitoring in rural areas has identified that the maximum oxidants recorded in rural and urban areas may exhibit different source-receptor relationships.

Recent field studies by the EPA in the Ohio Valley (5) and in the northern United States and Gulf Coast (30) have acquired data both in rural and urban areas. The studies show that the frequency of ozone concentrations exceeding the standards and the maximum ozone recorded in some rural areas is comparable to what has been found in urban areas, despite the fact that the local precursor emission base is relatively small. The transport of pollutant emissions from urban areas to rural areas is hypothesized as a link between urban and rural oxidant problems. Therefore, two different source-receptor relationships need to be developed to understand the effectiveness of the control of precursor emissions.

The scientific literature reviewed in the following sections will focus upon the source-receptor relationship between urban oxidants and urban precursors. The review will also look at long-range pollutant transport because the urban oxidant problem and the rural oxidant problem appear to be related.

SOURCE-RECEPTOR RELATIONSHIPS (URBAN AND NEAR URBAN AREAS)

Field Data

Investigations into the specific relationships between urban hydrocarbon and nitrogen oxide emissions and/or concentrations, and urban oxidants have been conducted extensively in recent years utilizing field data. Different field data gathering techniques were used to determine source-receptor relationships and are:

- Upwind and downwind monitoring of urban areas for O_3, hydrocarbons, and nitrogen oxides by fixed ground stations or airborne measurements;
- Trajectory analysis;
- Oxidant and emission trends.

Ground-based ozone monitoring data have been used to qualify and quantify the relationship between ozone, hydrocarbons, and nitrogen oxides. The national EPA strategy for the control of hydrocarbon emissions (Appendix J) was based on the hydrocarbon and ozone data recorded at CAMP monitoring sites across the United States (2). Recently, extensive use of both ground-based and airborne ozone data gathered by local, state, and Federal air pollution control agencies, and by the private sector, have been used to qualitatively assess the contribution of specific urban areas and their associated emissions on downwind ozone concentrations.

The effect of urban complexes on downwind ground-based ozone monitors was investigated in New York City by Rubino et al. (36) and Cleveland et al. (37), in Camden-Philadelphia by Cleveland and Kleiner (38), and in Chicago by Lyons and Cole (39). In all cases, elevated ozone concentrations were reported downwind of the urban complex. Cleveland et al. (37) also found that there was a shift of photochemical activity to later hours of the day with increasing distance downwind of New York. This determination was based upon the fact that the time of maximum ozone concentration progressed with increasing distance downwind of New York City.

A study conducted in Ohio by the Environmental Protection Agency (5) utilized both ground-level and airborne ozone measurements to assess the contribution of the emissions of specific urban areas on downwind ozone concentrations. Of the urban areas investigated, elevated ozone concentrations were recorded by ground stations and by airborne flights downwind. White et al. (40) also found elevated ozone concentrations above the ground, downwind of St. Louis, using data taken by aircraft.

Data contained in the reports reviewed above suggest a qualitative relationship between emissions of hydrocarbons and nitrogen oxides and ozone. In all cases, the concentrations of ozone recorded downwind of the urban complexes exceeded the upwind concentrations. In many cases, upwind concentrations of ozone were above 0.08 ppm.

Hydrocarbon and nitrogen oxide data recorded at monitoring sites simultaneously with ozone were used in the past, especially in the Los Angeles area (2), to relate ozone concentrations to hydrocarbon and nitrogen oxide levels. With recent evidence accumulating that broad geographic areas, especially east of the Mississippi, experience widespread high ozone concentrations, the thrust of recent field studies has been concentrated on the source-receptor relationship of monitoring sites in urban and rural areas. Field studies, such as the ones conducted in the Ohio Valley in 1974 (5) and in the northern United States and Gulf Coast in 1975 (30), have concluded that different source-receptor relationships exist between rural and urban areas. In urban areas, the concentrations of both ozone and precursor emissions are high, whereas in rural areas, the concentrations of ozone may be high but precursor emissions are low. In these EPA studies, both elevated ozone and hydrocarbon concentrations were found downwind of cities. The maximum concentration of ozone and hydrocarbons occurred at different distances downwind.

Studies completed in Texas by Walker (41) and Neal et al. (42) used 6 a.m. to 9 a.m. nonmethane hydrocarbons and recorded the maximum ozone concentrations to establish source-receptor relationships. Similarly, Huffman et al. (43) used 6 a.m. to 9 a.m. nonmethane hydrocarbons and nitrogen dioxide concentrations for Indianapolis. For these studies, results indicate a weak relationship between precursor emissions and maximum ozone concentrations.

Trajectory analysis has also been used to establish relationships between precursor emissions and maximum ozone concentrations. The EPA field studies reviewed earlier (5,30) utilized trajectory analysis and determined that the highest ozone concentrations measured in the studies can be attributed to principal cities or areas of high ozone precursor emissions. Meyer et al.

(20) performed a study using ozone data recorded at rural and urban locations. The correlation between local precursor emissions is significant and positive for the urban locations, and there exists a high degree of intercorrelation between HC and NO_x emissions. No apparent relationship between local, manmade precursor emissions and ozone is apparent at rural sites.

Data recorded from ambient ozone monitors over long periods of time has also been analyzed, where control strategies have been implemented for nitrogen oxides and hydrocarbons, to establish source-receptor relationships. In one such study, Trijonis et al. (15) compared the historical trends in oxidant concentrations in Los Angeles with trends in hydrocarbon and nitrogen concentrations and emissions. He concluded that improvements in oxidant air quality agreed well with the reductions in hydrocarbon emissions, and that NO_x emission increases may have contributed to the reduction by decreasing the HC/NO_x ratio.

From field data reviewed in this section, it appears that a qualitative relationship does exist between precursor emissions and the maximum oxidant concentrations recorded at urban sites. The correlation of hydrocarbons to maximum oxidant concentrations is better supported than the relationships between oxidants and nitrogen oxides. It appears, though, that there may be inherent limitations in correlating ozone data at specific monitoring sites with primary pollutants that may undergo complex photochemical reactions.

Based upon the evidence presented from the field data and considering that there are limitations to its use for control strategy development, the optimum strategy for oxidant reduction is the control of hydrocarbon emissions.

Lab Data

Earlier Smog Chamber Studies--

Before 1970, it was reported in the literature that several studies of

ultraviolet-irradiated hydrocarbon and nitrogen oxide mixtures had been conducted to simulate the production of ozone in the ambient air. The results of these studies, as reported in the criteria document for photochemical oxidants (2), show a dependence of oxidants on hydrocarbon concentrations in spite of the many differences in choice of initial reactants and experimental design. Initial hydrocarbon concentrations used in those studies ranged from 1.0 ppm C to 12.0 ppm C, and the composition of the hydrocarbon mixture was either automobile exhaust or propylene. A similar dependence of oxidants on nitrogen oxides was demonstrated in these smog chamber studies. Concentrations of nitrogen oxides ranged from 0.5 ppm to 1.0 ppm. These laboratory photooxidation experiments also suggest the existence of an optimum HC to NO_x ratio with regard to the maximum attainable oxidant, in addition to the dependence on the absolute concentrations of hydrocarbons and nitrogen oxides.

The maximum ozone produced in these laboratory studies (2) was within the range of the maximum hourly ozone concentration recorded at the CAMP monitoring sites located across the United States from 1964-1967. Similarly, the concentrations of the initial reactants irradiated were comparable to those concentrations of hydrocarbons (44) and nitrogen oxides (11) recorded in major cities in the United States. Although some of the initial reactant concentrations used in the smog chamber studies were within the range of ambient monitored levels, the majority fell outside of the range of ambient monitored values.

The application of the results of smog chamber studies to determine the control of photochemical oxidants was tested using the oxidant isopleths derived from laboratory experiments that showed the effect of varying initial precursor hydrocarbon and nitrogen oxide concentrations. In all cases, at every HC-NO_x concentration, reductions in hydrocarbons without NO_x reduction resulted in reduction of oxidants, whereas NO_x reduction without HC reduction did not always lead to a reduction of oxidants.

Recent Smog Chamber Studies--

Recent indoor smog chamber studies (45-47) have focused their attention

on specific interrelationships of the initial reactants of the photooxidized mixture, the duration and light intensity of the irradiation source, and the relative reactivity of the hydrocarbon mixtures. In all cases, the results have still yielded the dependence of oxidants on both hydrocarbon and nitrogen oxide concentrations. The results of smog chamber studies completed by Dimitriades (45) in which automobile exhaust was irradiated for a 6-hour period, indicate that the amount of ozone produced is dependent upon the HC/NO_x ratio of the irradiated mixture, and at higher HC/NO_x ratios the ozone produced in the chamber is maintained for a longer duration.

Powers (48) assessed the oxidant-formation potential of both catalyst-equipped and unequipped automobile exhaust mixtures irradiated over a 10-hour period. He found that the maximum ozone produced occurred using a hydrocarbon mixture representative of a vehicle without a catalyst. The results of the experiment also showed that hydrocarbon reactivity was a valid concept under experimental conditions. Other smog chamber studies by Glasson and Wendschuh (46) and Pitts et al. (47) have confirmed that hydrocarbon reactivity is important because hydrocarbon compounds, when irradiated, will show differences in the amount of ozone that can be produced and the time necessary to reach the maximum ozone.

To simulate the effect of atmospheric transport conditions, Glasson and Wendschuh (46) irradiated the initial reactant mixture under alternating 6-hour periods of light and darkness. Under these conditions, automobile exhaust produced the highest multiday maximum of ozone in a 3-day period. Similarly, the effects of atmospheric dilution were tested by Powers (48). The results of the dilution experiment indicate that reactivity differences are still discernable under the prolonged experimental dilution.

These smog chamber studies are representative of actual atmospheric conditions only to the extent to which the following conditions are satisfied:

- The interdependence of initial reactants and resultant oxidant levels are the same in the smog chamber as in the atmosphere.

- The composition of the initial hydrocarbons in the smog chamber are the same as in the atmosphere.
- The hydrocarbon to nitrogen oxide ratios of the initial reactants are the same as in the atmosphere.

Also, an important consideration is "dirty" chamber effects associated with man-made enclosures. Although the conditions in the atmosphere cannot be duplicated exactly in the smog chamber, these results can be used in a gross way to test the effectiveness of precursor emission control strategies for oxidants.

The smog chamber studies of Dimitriades (45,49) indicate that the control of precursor emissions is dependent upon the HC/NO_x ratio and that the control of hydrocarbons without NO_x control, no matter what the HC/NO_x ratio is, will result in an oxidant reduction. On the other hand, at certain HC/NO_x ratios, NO_x reduction does not always lead to a reduction in ozone without HC reduction. Dodge (10) developed a photochemical model and simulated the results of Dimitriades with good correlation. Extrapolation of these results regarding control strategy implications was tested. The results were similar to those of Dimitriades (45).

Most recently, outdoor smog chamber studies have been employed to simulate conditions of photochemical oxidant formation in the ambient atmosphere. The results of these studies show a similar dependence of oxidant concentrations on hydrocarbons, nitrogen oxides, and the HC/NO_x ratio as reported in the indoor smog chamber. In addition, experiments on the effects of multiday irradiation, dilution, and light intensity were tested.

In an outdoor smog chamber study performed by Sickles et al. (12), initial chamber reactants were irradiated for daylight periods and subjected to a period of dilution to simulate the movement of air from an urban to a nonurban area. The results of this study indicate that, in partially spent, simulated urban photochemical systems, ozone could be generated in concentrations above the NAAQS with low absolute NO_x concentrations and at high HC/NO_x ratios. The data also suggest that an ozone carryover exists, and that

this carryover may provide a high minimum on which to build a high maximum the next day. The carryover or halflife of ozone concentrations ranged from 20 to 30 hours.

The effect of light intensity was studied by Jeffries et al. (50), and results show that fluctuations in solar radiation, provided they are small, tend to accelerate a photochemical system giving higher rates of NO_2 and O_3 formation compared to results of experiments done when either constant or gradual changes in light intensity were applied.

The results obtained from indoor smog chamber studies are representative of the actual atmosphere only to the extent to which those conditions specified in the subsection on Recent Smog Chamber Studies are satisfied. Concentrations of the initial chamber reactants in these studies ranged from 1.0 ppm C to 7.0 ppm C of hydrocarbons and 0.10 ppm to 1.0 ppm of NO_x. Propylene was used as the hydrocarbon irradiated in the experiments done by Jeffries et al. (50), and a surrogate urban mixture of hydrocarbons was used by Sickles et al. (12). The fact that outdoor smog chambers are irradiated in natural sunlight and are subject to natural variations of the light intensity profile makes outdoor smog chamber studies inherently more closely related to the simulation of air parcels in the urban environment. In addition, it has been reported (50) that the heterogenous reactions (dirty chamber effects) are less significant in these experiments due to the large Teflon chambers.

The results of these outdoor smog chamber experiments have introduced some important implications for control of precursor emissions. These results are:

- The half-life of ozone being 20 to 30 hours, the ozone carryover may produce a high minimum on which to build a high maximum. This carryover may occur locally, or it could be transported downwind to provide a high minimum for another urban area.
- A mechanism has been provided to explain one source that may contribute to high ozone in rural areas. This mechanism suggests that the emission carryover of a photochemical oxidant system could cause the production of ozone above the NAAQS with low absolute NO_x concentrations and at high HC/NO_x ratios.

These results imply that the amount of precursor emissions to be controlled must go beyond the amount that is necessary to alleviate the local urban oxidant problem. Both locally generated emissions and oxidants may provide a significant carryover that can either provide the local downwind urban area with a high ozone minimum or a sufficient amount of emissions on which to build a higher maximum ozone concentration or both.

Comparison of Outdoor-Indoor Smog Chamber Studies--

The results of those indoor and outdoor smog chamber studies reviewed in the subsection on Recent Smog Chamber Studies show a dependence of oxidants on hydrocarbon concentrations in spite of the many differences in experimental design. In addition, indoor (46,47) and outdoor (9) studies have shown a dependence of oxidant concentrations on individual hydrocarbon compounds. The composition of the initial hydrocarbon mixture used in both indoor and outdoor smog chamber studies varied, with propylene and auto exhaust being the prime initial smog chamber reactants. Similarly, the dependence of oxidant concentrations on nitrogen oxide has been demonstrated in both chamber environments, although the rates of NO_2 formation have been reported (50) to be higher due to natural light intensity effects in outdoor smog chambers.

Dimitriades (45) demonstrated in an indoor smog chamber that ozone was dependent upon the HC/NO_x ratio of the initial chamber reactants and that ozone produced in the chamber is maintained for a longer duration. Also, in an outdoor smog chamber study done by Jeffries et al. (9) in which a synthetic urban mixture of acetylene, paraffins, and olefins were used, the maximum ozone produced increased proportionately to the increase in the initial HC/NO_x ratio of the chamber.

The maximum ozone produced in both chamber environs compare favorably, although the experiments of Jeffries et al. (50) indicate that at higher HC concentrations, the maximum ozone produced in outdoor smog chambers exceeded the amount formed in those indoor studies done by Dimitriades (45). Jeffries et al. (50) say that the effects of natural light intensity are the cause of the differences observed.

In comparing the results of indoor and outdoor smog chamber studies as to their representativeness of air parcels in the urban environment, it appears that outdoor smog chamber studies simulate atmospheric conditions more closely for the following reasons:

- As reported by Jeffries et al. (50), the use of large Teflon chambers appears to reduce dirty chamber effects, which may be a significant factor in indoor chamber studies.
- The irradiation of HC-NO_x mixtures in the presence of natural sunlight results in a better approximation of the photooxidation process in the ambient air.

It appears that outdoor smog chamber studies provide a better understanding of photochemical systems and allow a better extrapolation of their results to real world situation. However, extrapolation of indoor and outdoor smog chamber results to the control of precursor emissions do not yield significantly different results. Only a few of the papers reviewed deal directly with the quantitative implications of the control of precursor emissions on reduction of photochemical oxidants. The data implies that the reduction of hydrocarbons in all cases will reduce urban oxidant concentrations, whereas the reduction in nitrogen oxides may have an effect depending upon the HC/NO_x ratio. Therefore, from the results obtained by smog chamber data, the optimum control of urban oxidants can be achieved by a reduction in hydrocarbon emissions. Of course, the degree to which urban oxidant reduction can be achieved by the control of local hydrocarbon emissions, as determined by both indoor and outdoor smog chamber data, is dependent upon whether ozone concentrations in an area are significantly affected by nonlocal sources.

Lab and Field Data/Oxidant — HC/NO_x Relationships

The field data and lab data have been reviewed to assess whether quantitative and qualitative relationships exist between anthropogenic emissions of hydrocarbons and nitrogen oxides and oxidant concentrations in the ambient air. The review was conducted to evaluate whether the relative evidence presented by the field and lab data support the original hypothesis that hydrocarbon reduction is the optimum urban oxidant control strategy.

As discussed in the subsection on Field Data, the field data does show evidence that a qualitative relationship exists between hydrocarbons and oxidant concentrations particularly in urban areas. This qualitative relationship is supported by the fact that there exist elevated ozone concentrations downwind of major urban complexes which exceed upwind concentrations. Although downwind monitoring does suggest a positive relationship, the correlation of ozone concentrations with hydrocarbon and nitrogen oxide data recorded at the same monitoring site on a diurnal time frame has been marginal, at best. Correlations of this type, though, may be limited because of the complexities associated with relating primary and secondary pollutants under dynamic atmospheric conditions in a short time frame.

Long-term trends of oxidant, both in the Los Angeles area (15) and in major cities of the United States (16), have been significantly related to trends in hydrocarbon emissions. In addition, Martinez et al. (16) found the combined HC-NO_x emission trends to be more significantly correlated than HC alone.

The evidence presented by the field data tends to support the conclusions that the control of hydrocarbons alone is the optimum urban oxidant control strategy. The selection of the control of hydrocarbons only is based upon the fact that more scientific evidence presented in field data supports hydrocarbon reduction, whereas the effects of NO_x reduction may cause as yet undetermined and inconclusive effects upon oxidants.

Lab data, particularly that derived from both indoor and outdoor smog chamber studies, has qualitatively and quantitatively established relationships between hydrocarbons, nitrogen oxides, the ratios of HC to NO_x, and oxidants, in spite of the many design differences associated with these experiments. Indoor smog chamber studies, particularly those of Dimitriades (45), have been used to postulate relationships between the control of oxidants and reductions in hydrocarbon and nitrogen oxide emissions. These data suggest that the control of hydrocarbons at any combination of HC-NO_x concentrations will cause a reduction in oxidant concentration, whereas the

effect of NO_x control is dependent upon the HC/NO_x ratio and, therefore, is highly speculative.

Although the evidence strongly suggests that control of hydrocarbons alone may be the optimum urban oxidant control strategy, Dimitriades (45) cautions that the extrapolation of his results may be valid only so far as the chamber environment represents ambient conditions. The effects of the chamber itself, plus the fact that most indoor chamber experiments have been conducted using both hydrocarbon concentrations, individual hydrocarbon compounds, and nitrogen oxide concentrations which may be unrepresentative of ambient air, introduces an element of speculation into the extrapolation of chamber results to real world situations. Outdoor smog chamber studies have duplicated the results obtained from indoor studies and in addition, as Jeffries et al. (50) report, chamber effects have been minimized.

Considering the fact that both outdoor and indoor smog chambers can only approximate the real world, the results still indicate qualitatively that control of hydrocarbons is the optimum urban oxidant strategy. Although the effect of NO_x in the chamber can be demonstrated, its effect on oxidant can be different depending upon the chemical balance (HC/NO_x) of the ambient air. The extrapolation of NO_x effects in the chamber to the ambient air at this time would be inappropriate without further studies to support NO_x effects over all possible cases to be expected in the ambient air.

The precursor control implications, as determined from field and lab data, support the fact that hydrocarbon control is the optimum urban oxidant control strategy. The selection of this strategy, though, is better supported by lab data than field data at this time.

Recommendations — Oxidant Control Strategies

Based upon our judgment of the evidence presented in the review of field and lab data, the optimum strategy for urban oxidant reduction is hydrocarbon emission control. As far as the urban oxidant problem is concerned, it is our recommendation that NO_x control is tolerable when scientific evidence is considered but undesirable from an implementation standpoint.

The discussions below are intended both to qualify the recommendations made and to touch upon other topics that were considered in arriving at the recommendation. Also included are general suggestions of research that may help to explain further the complex photochemical relationships associated with the urban oxidant problem.

Hydrocarbon Control--

The most recent scientific evidence tends to support continuation of hydrocarbon reduction as an effective strategy. The most promising reports are those of apparent oxidant reduction paralleling the HC reduction in Los Angeles (15). The word "apparent" is used because long term urban sampling may have been subject to changes in instruments, methods, site locations, instrument height, probe materials, local changes in alkenes and NO_x, seasonal changes in temperature and solar radiation from year to year, increases in data quality control efforts, and recently discovered problems in calibration.

Smog chamber data support the trends detected in Los Angeles; i.e., control of hydrocarbons should, in general, reduce oxidants. The agreement between the field and lab data in this situation, though, must be qualified because, to a certain degree, the meteorological regime existing in Los Angeles approximates the simulation of a confined air mass that exists in a laboratory smog chamber. The Los Angeles area, though, is geographically unique and is quite different from the vast areas to the east of the Mississippi.

Field studies in the Northern United States and Gulf Coast (30), the Ohio Valley (5), and the Great Lakes (39) have identified different macroscale and mesoscale meteorological situations under which high ozone episodes may occur. The extrapolation of the lab and field data, which represent relatively confined air mass situations, to these areas may not be quantitatively representative because of the complex source-receptor relationships. Although the quantitative relationship may be different under different meteorological regimes, the data still supports the fact that hydrocarbon control is the optimum urban oxidant control strategy.

In addition to the field and lab data presented, hydrocarbon control is desirable from the technological standpoint, since advances in hydrocarbon control are much further ahead than those for NO_x control. There is also some merit in focusing control on only one pollutant, namely hydrocarbons, from an implementation standpoint. Reductions in hydrocarbons are already being achieved through the Federal Motor Vehicle Emission Control Program. The combined effect of mobile source and new point source controls could result in large reductions of hydrocarbons within a reasonable time frame. Directing emission control efforts to the pollutant that will cause the most demonstrable effect on oxidants and in the shortest time frame is the best approach to oxidant control.

Nitrogen Oxides--

As discussed in the subsection on Field and Lab Data, NO_x plays a significant role with respect to the production of ozone concentrations, but the effect of NO_x reduction is very dependent upon the HC/NO_x ratio and the absolute concentrations of these precursors in the ambient air.

Presently, not much is known about the ambient HC/NO_x ratios in either cities or rural areas. The control of NO_x will adjust urban and rural HC/NO_x ratios with as yet unknown effects on oxidants. When all oxidant reductions from hydrocarbon control have been achieved, it may be necessary to implement NO_x control. Considering the scientific evidence presented, NO_x control is tolerable. Although NO_x control may be tolerable, it is desirable to postpone NO_x controls from the standpoint of implementation. Presently, there are too few new, controllable, point sources to make any but a negligible impact over a long period. Also, the control technology for NO_x is far behind that of hydrocarbons. As discussed before, it is more practical to focus control on the pollutant that would achieve the largest oxidant reductions in the shortest period. The evidence presented from both the field and lab studies indicates that the pollutant that would achieve those positive results is hydrocarbons.

Research--

The review of both lab and field studies has indicated that there are still deficiencies in applying the data gathered to the quantification of oxidant reduction to be achieved by HC and NO_x control. Of the EPA field studies completed to date, the main emphasis has been directed toward characterizing the ozone problems in broad geographic areas. The results of these studies have identified that both rural and urban areas have different source-receptor relationships. Since national EPA policy is leaning towards the control of urban precursors as the first step in attaining the NAAQS for oxidants, additional research is recommended that deals directly with the complex source-receptor relationship of individual cities.

Specific recommendations for additional research are:

- Further investigate the feasibility of simulating continental ozone problems through chamber experiments using appropriate dilution and reradiation experiments so as to simulate transport situations.
- Using chamber experiments, determine the ozone yields of ambient air containing representative concentrations of hydrocarbons and nitrogen oxides.
- Where different meteorological regimes impact the source-receptor relationship of broad geographic areas, intensively study representative cities within that area to determine relationships among ozone, hydrocarbons, hydrocarbon compounds, and nitrogen oxides. Chamber studies could possibly be conducted simultaneously with the data acquisition effort.

These specific recommendations for additional research may help to clarify the source-receptor relationship in urban areas and ultimately provide additional data to aid in the design of State-level control strategies for the control of oxidants.

QUANTITATIVE EVALUATION

In the preceding sections, lab and field data were discussed in terms of the directional impacts of oxidant control. It was recommended, after a

review of the pertinent scientific literature, that the optimum strategy for urban oxidant reduction was the control of hydrocarbon emissions. In the following sections, four different approaches will be discussed evaluating the quantitative impacts of hydrocarbon control in terms of the relationship between ambient oxidant concentrations and emission control, and the relationship between the source area and receptor area. Each approach will be discussed individually and collectively in terms of its relative advantages and disadvantages. The discussion will be focused upon a "cause" and "effect" relationship with a "source area" and "receptor area," respectively, defined as the area where hydrocarbons are emitted and the area where air quality is being impacted.

Approach I

The approach proposed for consideration here is identified with the cause of the maximum oxidant concentration in the "receptor area," due to both local and upwind emissions in the "source" area. This approach requires that all the source areas impacting upon the receptor area be identified and that the impact of upwind emissions be quantitatively evaluated to determine the amount of oxidants being contributed from upwind sources. For large urban complexes which are isolated from upwind influences, such as Los Angeles, this approach may be feasible but for an area such as the northeastern United States where many cities may have influence upon the air quality of others, this approach could involve a major research effort. It is not, however, impossible.

Upwind influences of emissions on worst case oxidant days could be accomplished by identifying the source areas by trajectory analyses and quantifying their influence by applying one of the state-of-the-art photochemical models. The results obtained from this exercise, though, could be quite speculative considering the fact that smog chamber data (12,46) and field studies (5,30) have indicated that both emission and ozone carryover may be a significant factor in contributing to second-day high minimums on which a high maximum can be produced. The effect of carryover from one urban area to the next may underestimate the effect of other urban areas on the local urban oxidant problem and, hence, cause more local control to be imposed.

Considering the time and effort that may be invested in this work and the fact that the results may be speculative, this approach is not very advantageous.

Approach II

This approach considers the fraction of the observed maximum oxidant concentration as the effect. The cause is identified with the local emissions. Application of this method to determine the degree of local emissions control requires that ozone be obtained from an upwind and a downwind receptor so that a maximum oxidant fraction can be estimated. The assumptions that are made when determining the maximum oxidant fraction are:

- That the upwind and downwind receptors are situated so that chemical and physical interferences are minimal. For example, if the upwind monitor is being influenced in some way by *local* NO_x emissions, the maximum oxidant fraction calculated would be erroneously high. In other words, the fraction of oxidant due to local emissions would be high, and more local control of hydrocarbons would be required.
- That the fraction of the maximum oxidant estimated does not contain any oxidant produced by extraneous upwind emissions; i.e., the fraction of maximum oxidant estimated is only due to local emissions.

The problem of site monitoring referred to in the first assumption can be solved partially by careful placement of monitors so as to minimize physical and chemical interferences. The second assumption, though, presents some complications.

The fraction of the maximum oxidant concentration across the urban area, estimated from measurements at the two receptors, may be the result of both extraneous and local emissions. The upwind and downwind monitors should be sited so that the *maximum oxidant fraction* across the urban area is being measured. Also, the downwind monitoring site should be placed at a location where local emissions will produce their maximum oxidant concentration. Even if the siting problem could be solved, the problem of quantifying the indi-

vidual contribution of oxidants from local and extraneous emissions still exists.

Although there are some serious disadvantages to this method, especially for large cities grouped together, it could be applied to urban areas that are not being substantially affected by extraneous emissions. From recent field studies, urban plumes of major cities have been tracked out to 100 km. A criterion for application of this method might be that the urban area would have to be outside of a 100-km radius of another major urban area.

Approach III

The third approach is identified with the "effect" being the maximum oxidant concentration observed in the receptor area and "cause" being the "local" emissions. This method is another reiteration of the Appendix-J method, since it specifies that control be confined within the urban area where the oxidant problem was observed. The assumption that this method agrees with is that local emissions are the sole contributors to the local oxidant problem. It also neglects the importance of emission and/or oxidant transport.

The obvious disadvantage of this method is that application of controls calculated by this approach will result in over-control in the source area. It has been argued, though, that the disadvantage in actuality is not necessarily a problem because the sum total of the "local" and "transported" contributions may exceed the 0.08 ppm standard, even though individual contributions are less than 0.08 ppm. In addition, it has been argued that local emissions almost surely contribute to or add additional problems to downwind areas.

To clarify the differences in opinion offered in the evaluation of this approach, an example is provided that will illustrate the use of this approach in Wisconsin.

Figure 1 is a graphical layout of the urban complex associated with the areas of southeast Wisconsin, northeast Illinois, and northwest Indiana.

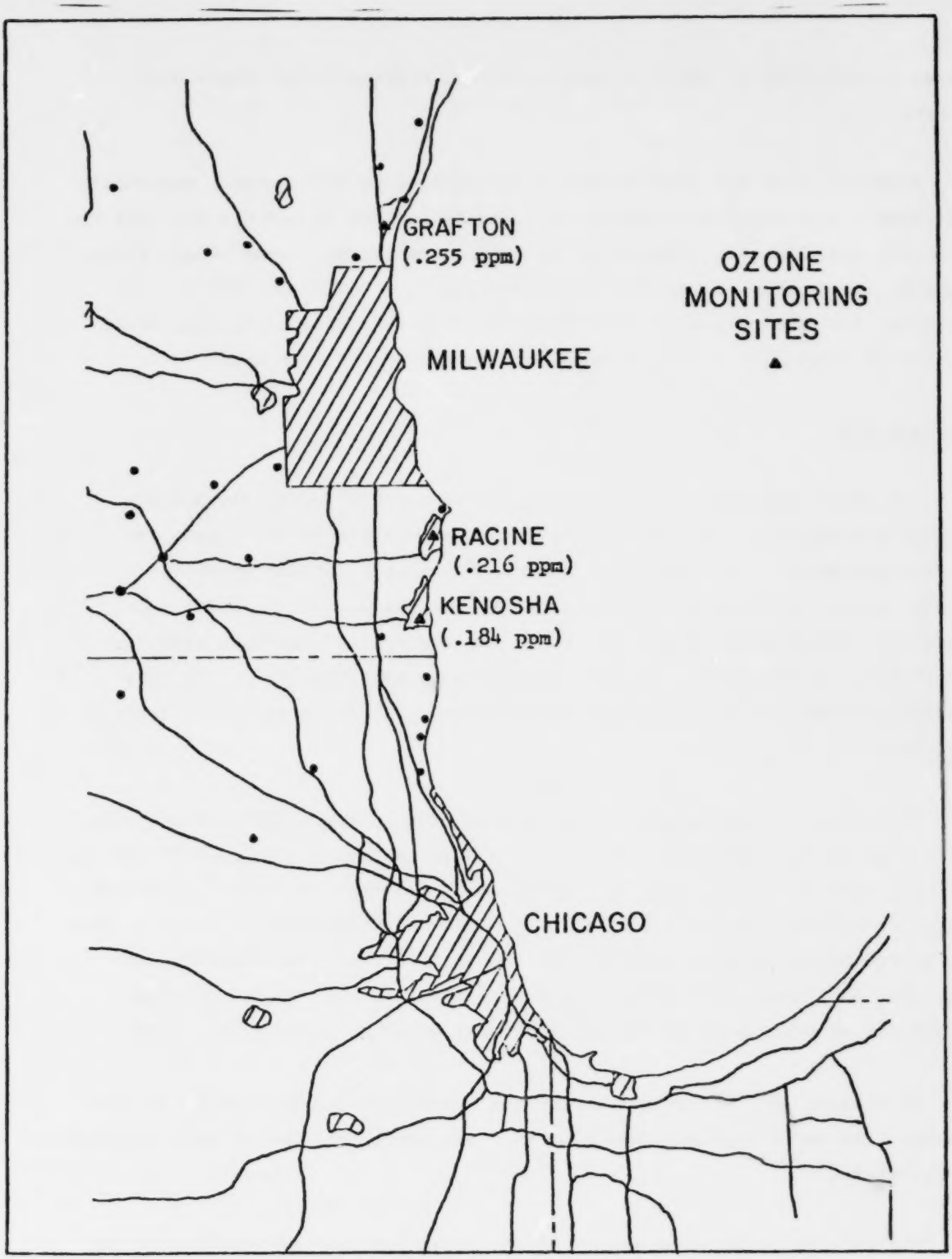

Figure 1. Maximum hourly ozone concentrations recorded at monitoring sites in Southeastern Wisconsin on August 20, 1976.

Plotted on the map are the maximum oxidant values recorded at three monitors in southeast Wisconsin for August 20, 1976. Meteorological conditions associated with these high oxidant values were characterized by sunny skies, moderate wind speeds, and wind direction from southwest through southeast.

For discussion purposes here, let us assume that these concentrations were the maximum oxidants measured that year. Applying the methodology of Approach III, the maximum concentration of 0.255 ppm would be used to calculate the necessary oxidant reduction for southeast Wisconsin, i.e., the Milwaukee urban complex. In this case, the amount of hydrocarbon control would be based upon eliminating a fraction of 0.175 ppm oxidants even though the sites upwind of Milwaukee are approximately 0.20 ppm. As is the case when most ozone concentrations recorded in southeast Wisconsin exceed 0.08 ppm, transported ozone dominates the local urban situation. Therefore, it would not be applicable to apply this control method to situations where the transport dominates the local problem, as reported in northeast states by Rubino et al. (36) and Cleveland et al. (37). Although the calculation of hydrocarbon by this method may not be valid in transport-dominated areas, the argument that local emissions cause additional problems in downwind areas is valid and cannot be neglected.

Approach IV

In this approach, the fraction of the maximum oxidant concentration is defined as the "effect" and local emissions as "the cause." The methodology proposed here is similar to that of the second approach but acknowledges the fact that increased control of local emissions may be necessary to offset a contribution from upwind sources. In other words, each urban complex would be required not only to achieve 0.08 ppm, but to control its emissions further to offset extraneous upwind emissions.

No method for estimating the necessary oxidant fraction to offset extraneous sources is proposed in addition to the arguments already expressed in the subsection on Approach II. Therefore, some criteria must be developed to account for the offset required. This additional amount of control should

not, of course, be based on the values recorded at the upwind monitoring site but on a prescribed offset, for instance 0.02 ppm. The prescribed offset eliminates any possible problems that may exist, especially those that may arise from the interstate transport of pollutants, since transported air from each urban complex would be cleaner than the standards.

Comparison of Approaches

The control strategies reviewed in the previous sections can be separated into two general categories. Approaches I and III relate the maximum oxidant concentration to the "effect" and either local and/or upwind emissions to "cause." Approaches II and IV relate the fraction of the maximum oxidant concentration to the "effect" and local emissions to the "cause." The advantages and disadvantages of each approach have been discussed individually. This discussion, therefore, will focus on whether any of these approaches will be recommended as a strategy for urban oxidant reduction.

The goal of any air pollution control strategy is to control pollutant emissions in the most equitable manner possible, i.e., source reduction equated to source contribution. The quantitative evaluation of source contribution is the crux of the entire photochemical oxidant control issue. The four different approaches that have been reviewed propose ways in which local emission control can be determined in terms of how locally measured oxidants relate to both extraneous and local emissions.

All of the approaches except III focus on ways of evaluating the contribution of local and extraneous emissions to the local urban oxidant problem and obtaining local control of emissions. Approach I requires that all source areas affecting the receptor be identified, and Approach II separates all source areas into two categories, local and extraneous. In a sense, Approach II is the same as I because all source areas other than local sources are considered collectively and identified as extraneous. Although Approach I uses the maximum oxidant observed in the receptor as the "cause," it still proposes to evaluate the individual contributions of each source; therefore,

the fraction of maximum oxidant observed is implied as the determination for local control, as in Approach II.

The fourth approach utilizes the fraction of the maximum oxidant concentration as a means of determining local control but implies that further local control may be necessary to offset extraneous emissions. This approach differs from I and II only in terms of the degree local control must be implemented. It addresses the situation where the local receptor may be above 0.08 ppm, even after local control has been implemented. In terms of the basic design of determining the degree of local emission control, Approaches I, II, and IV are similar except that Approach IV recommends additional local control to offset the effect of extraneous emissions.

Approach III is very different from all other approaches proposed because it treats extraneous emissions in a qualitative manner. The maximum oxidant observed in the receptor area is used to determine local control of emissions to achieve the standard. The argument presented supporting this approach is that although extraneous emissions are recognized as a factor, local emissions still contribute to a downwind problem. Even considering the fact that local emissions do add to downwind concentrations, Approach III cannot be considered as the optimum oxidant strategy for the following reasons:

- Recent scientific evidence has clearly demonstrated that extraneous emissions are an important factor in control strategy development.
- The quantitative effect of extraneous emissions is eliminated as a decision-making tool to local hydrocarbon control.
- Although local emission control may have to go beyond the amount necessary for control to attain 0.08 ppm, the quantitative effect of local emissions is eliminated as a decision-making tool to local hydrocarbon control.
- In most cases, use of this method will result in an inequitable degree of local emission control.

Of the three control strategies remaining, Approach IV provides the best method for quantifying the degree of local hydrocarbon control necessary be-

cause both Approach I and II have obvious disadvantages. Approach I relies on many theoretical assumptions to identify the effects of individual source areas on the maximum oxidant. These assumptions introduce too many variables on which to quantify local hydrocarbon reduction. The second approach, although basically sound, only considers the control of local emissions to reduce the fraction of maximum oxidant observed to 0.08 ppm. Calculating control requirements to reduce the fraction of the oxidant down to 0.08 ppm obviously will not solve the problem.

The control strategy proposed in Approach IV has been selected for the following reasons:

- The effect of extraneous emissions and local emissions using *actual* ozone monitoring data is quantified.
- The maximum observed fractional oxidant concentration is used to quantify the local hydrocarbon reduction necessary.
- Control of local emissions beyond that required to reduce the local oxidant fraction is recognized.

Although Approach IV is considered the best of the four reviewed, it is not recommended as the optimum oxidant strategy because problems associated with quantifying local hydrocarbon control still exist. The issue of estimating the fractional contributions of ozone from local and extraneous emissions is unresolved, and there is no quantitative method to determine the additional fraction of hydrocarbon control necessary to create an offset.

Therefore, certain modifications are proposed for consideration to be included in Approach IV as the recommended optimum urban oxidant control strategy. The modifications are:

- Hydrocarbon monitoring should be considered at locations upwind and downwind of urban complexes so as to relate increases of ozone downwind of cities to increases in overall hydrocarbons downwind of cities. This monitoring may clarify whether the elevated ozone concentrations downwind of cities are due to local emissions or to a photochemical peaking of extraneous emissions.

- A prescribed oxidant goal of 0.06 ppm be set in urban areas so that advected air arriving at the upwind urban monitor of an adjacent urban area will be cleaner than standards.

- No local hydrocarbon control for an urban area be required if the fraction of oxidants due to local emissions is determined to be less than 25% of the oxidant standard.

The decision to include these modifications to Approach IV was based upon evidence presented both in the field and lab data reviewed and also upon our judgment of how an equitable allocation of hydrocarbon emission reduction can be achieved. The proposed hydrocarbon monitoring was recommended after examining the hydrocarbon and ozone data obtained from surface ground measurements and aircraft upwind and downwind of Columbus, Ohio, in the 1974 summer ozone study (5). The data indicates that increases in hydrocarbon concentrations downwind of the city can be qualitatively correlated with the increases in ozone. Of particular importance is the fact that the ozone peak occurred farther downwind than the hydrocarbon peak. The small number of experiments of this type, though, limits the quantitative relationship that could be derived. Longer term evaluation of this type of data might be obtained from the monitoring program suggested for inclusion in Approach IV. The data obtained may be used to evaluate the individual contributions to the fraction of maximum oxidant measured across the city. A suggested approach would be to quantify the oxidant and hydrocarbon fraction across the urban area.

If both the hydrocarbon and ozone data show significant increases downwind of the urban area, then the local emissions may be the predominant contributor. In contrast, if ozone increases occur downwind of the city and hydrocarbons show no significant increases, the oxidants measured downwind are probably due to peaking of the extraneous upwind emissions. Using criteria developed from the monitoring program, the term "significant" can be quantified so as to establish meaningful interpretations of the data.

The second and third modifications suggested are very closely interrelated. It has been demonstrated to some degree by the scientific evidence presented that extraneous emissions from urban areas may affect the air quality of

others. The lab data particularly has implied that either carryover ozone, or emissions, or both may help to provide areas downwind with high minimum concentrations on which local emissions could build high maximums. This implies that the control of oxidants by individual urban areas to obtain the standard may prevent the standards from being attained because of the additive effects that may occur when urban areas are situated close to each other. Therefore, an oxidant goal of 0.06 ppm is suggested so that advected air cleaner than the standard arrives at the upwind urban site. This offset then would allow a smaller city, as alluded to in the third approach, to contribute 0.02 ppm and still prevent the oxidant standard from being violated. One may argue, though, that the air advected from the smaller city is providing air to another urban area at the standard. Is it, though, an equitable allocation of emission reduction to require the smaller city to reduce its local emissions totally to prevent an air quality violation, whereas the larger urban area is contributing a larger share of the problem? The requirement for no local control below 0.02 ppm was also suggested to account for the fact that there do exist limitations in the monitoring of ozone itself.

The modifications suggested in Approach IV are recommended to accomplish two purposes:

- To better quantify the contribution of local emissions so as to calculate local hydrocarbon reduction.
- To achieve an equitable allocation of hydrocarbon emission reduction.

The optimum urban oxidant strategy recommended is, therefore, Approach IV including the modifications suggested.

Recommendations

As discussed in the preceding section, Approach IV and the suggested modifications to it are recommended as the optimum urban oxidant control strategy. These proposed modifications recommended that hydrocarbon data be obtained from monitoring sites upwind and downwind of cities, that a prescribed oxidant offset be quantified to account for extraneous upwind emis-

sions, and that no local control of emissions be required if the local oxidant fraction is less than 25% of the national standard or 0.02 ppm.

Of the three modifications suggested, the proposal to monitor hydrocarbons may impose some difficulties at both the state and national level. No long-term hydrocarbon data are available for the majority of urban complexes in the United States. It would, therefore, be at least 2 years before hydrocarbon data could be utilized in a meaningful program of quantifying local emission reduction. In the interim period, though, quantifying the local oxidant fraction could be done with the upwind and downwind oxidant receptors. The recent scientific evidence presented in lab and field studies, which were reviewed in this report, qualitatively support the urban oxidant strategy that was recommended. The scientific basis for the support of this strategy or any other strategy, though, is very marginal. Additional research in the forthcoming years should be focused upon accumulating data that can be practically applied to the development and support of state and national level oxidant strategies. As recommended in the subsection on Recommendations — Research, the likely support and acceptance of the strategies by state and local air pollution control agencies is dependent upon strong and accepted scientific evidence, particularly where the application of controls is not very cost-effective.

REVIEW AND ANALYSIS

Frank Spuhler and Ken Waid

An optimum oxidant control strategy must recognize the photochemical mechanisms that produce ozone since ozone is the pollutant used to determine compliance with the national ambient air quality standard. First, it is important to note that the input reactants (precursors) into the system include: hydrocarbons (HC) (i.e., all organics, derivatives and specie as intermediate products), nitrogen oxides (NO_x), carbon monoxide (CO), water vapor, and sulfur dioxide (SO_2). For the most part focus has been only on HC (organics), leaving out the role of the other precursors. Carbon monoxide and nitrogen oxides produce ozone even when HCs are not present.

Of greater importance is recognition of the basic NO_2-NO-O_3 cycle that results from photolysis and establishes an equilibrium concentration of ozone in the absence of any other precursor emissions. This is stated as follows:

$$[O_3] = (0.021 \text{ ppm}) \frac{[NO_2]}{[NO]}$$

Figure 1 illustrates this cycle. The dominant factor in these systems is the ratio of nitrogen dioxide to nitric oxide. The challenge, then, is to explain the conversion of nitric oxide to nitrogen dioxide. Once that is done, the ozone concentration will follow the $[NO_2]/[NO]$ ratio (51).

> The oxidizable pollutants — such as hydrocarbons, aldehydes, and carbon monoxide — serve the function of regenerating free radicals that will react with the oxygen in the air to form alkylperoxy and hydroperoxy. Thus, these oxidizable pollutants can be thought of as pumping the nitric oxide to nitrogen dioxide. In the process, they become degraded to other compounds, some of which are still reactive (e.g., formaldehyde, CH_2O, and others). The amount of

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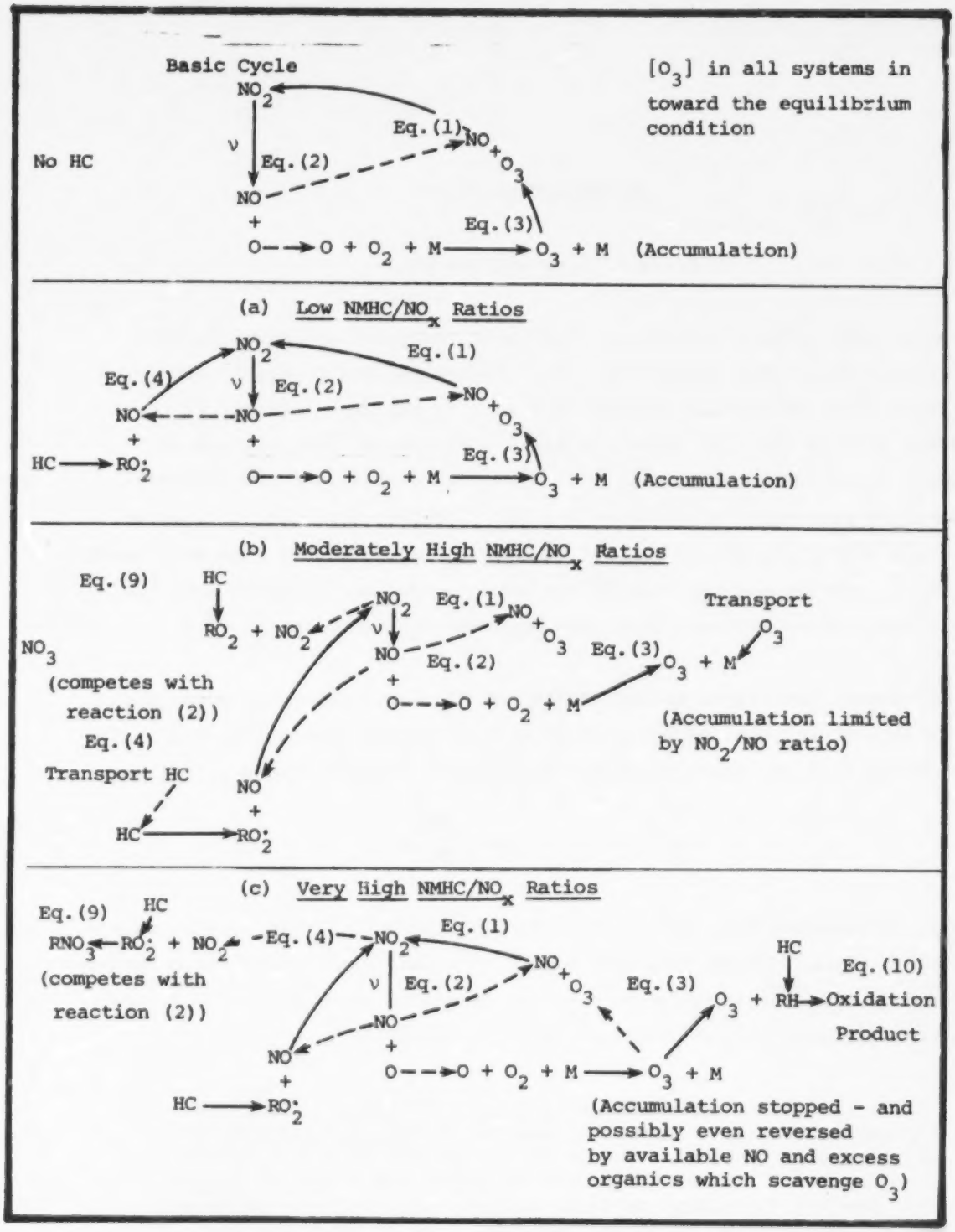

Figure 1. Schematic relationships among oxidant and precursors under low, moderate, and high NMHC/NO_x ratios (52).

> pumping that can be done, and thus the amount of photochemical oxidant formed, depends on both the reactivity of the oxidizable pollutant and its concentration in a nonlinear way. As the oxidant concentration builds up, the probability of ozone's reacting with hydrocarbons and various free radicals increases, and the rate of ozone accumulation decreases. Therefore, the major primary pollutants of importance to oxidant formation are nitric oxide, hydrocarbons, aldehydes, and carbon monoxide. A few free radicals are formed by photolysis of aldehydes and nitrous acid by sunlight or by the reaction of traces of ozone with reactive hydrocarbons. These free radicals initiate chain reactions involving hydroperoxy and alkylperoxy radicals. During these chain reactions, the nitric oxide is converted to nitrogen dioxide, and the hydrocarbons and aldehydes are degraded. The photolysis of nitrogen dioxide by sunlight forms a free oxygen atom, which combines with an oxygen molecule to form ozone. Because of the $NO\text{-}NO_2\text{-}O_3$ cycle, the ozone concentration is determined primarily by the ratio $[NO_2]/[NO]$ and so does not become large until most of the nitric oxide has been converted to nitrogen dioxide. The total amount of oxidant formed depends, in a nonlinear fashion, on the amount of hydrocarbons available to continue pumping the nitric oxide to nitrogen dioxide. Aldehydes and even carbon monoxide can also serve this pumping function. When some of the peroxy radicals recombine or react with the nitrogen oxides, many secondary products, such as hydrogen peroxide and PAN, are formed (52).

From these considerations, one concludes that present oxidant control strategies have not done a very good job in following the basic chemical laws involved in this dynamic mechanism. We have not included all of the reactants (precursors) and have oversimplified the applications that might indicate where the harmful dosage level of oxidant concentrations can be expected. EPA has stated that reductions of carbon compound emissions have reduced ozone emissions; however, in several of these cases there has been an increase of nitrogen oxides. The nitrogen oxide emission increases were not considered. It is, therefore, necessary to reexamine the entire oxidant issue to determine a realistic control strategy.

Although the photochemical oxidant pollution problem has been recognized for several decades, the nature, extent, and magnitude of the problem have been poorly defined. The data base is meager. We treat only part of the precursors. We leave out transport, mixing, and all that they imply. We have only spotty sampling data. We are not rigorous in our measurements and in measurements definition. Our knowledge of true health effects is superficial

and our correlations are sloppy. Reviews in all areas recommend more research and better problem definition.

The evidence presented at the International Conference on Oxidant Pollution and Its Control indicates that hydrocarbon emission control alone is not an optimum approach to solving the urban oxidant problem.

Some field studies showed HC control to have a strong beneficial effect, others did not show a detectable effect, and, others showed effects varying with attendant NO_x emission change. Smog chamber studies showed that for that portion of oxidant formed from the day's local emissions, control of HC is beneficial except for atmospheres with extremely high — ordinarily not observed — hydrocarbon-to-NO_x ratios; for such atmospheres HC control, unless drastic, will have very little effect. For that portion of oxidant formed through multiday irradiation of emissions, the evidence is considered scant and inconclusive by some investigators but conclusive by others. Those who feel that the evidence is conclusive claim that HC control will have small effects upon multiday, irradiated air masses, relative to the effect upon single day, irradiated air. Control of HC emissions upwind, again, has little effect according to some investigators, undetermined effect by others. While it is certain that the effectiveness of the HC control approach is different for different localities, the judgment called for is to recognize that different areas have different concentrations of the precursors for oxidant formation, and the same control strategy applied everywhere will not give consistent results.

NO_x is a precursor to oxidant formation and should be controlled. The data base and the present research are meager, and control strategies must address all precursors to oxidant formation.

The optimum control strategy for the oxidant problem should be application of Reasonably Available Control Technology (RACT) to both carbon compound emissions and NO_x emissions. The control strategy should state that there are no techniques at the present time to quantify the effects of the reductions.

The control strategy should not require any attempt to show a quantitative relationship between ambient oxidant concentrations and emission rates or a definitive relationship between source area and receptor area. The overall conclusion of all research on the oxidant problem today is that the data necessary to quantify the relationships between sources and receptors does not exist.

REVIEW AND ANALYSIS

Lee E. Jager

Reference is made to the paper entitled "International Conference on Oxidant Problems: An Analysis of the Evidence/Viewpoints Presented. Part I: Definition of Key Issues (1)." That paper identifies as one of the key issues "The Issue of the Optimum Oxidant Control Strategy" and within that issue asks several specific questions. My discussion will begin by responding to those specific questions; however, I do not believe that the optimum control strategy can be identified merely by answering those questions. Therefore, an additional discussion is also provided.

The first question asked is: Is the qualitative basis of the oxidant control strategy still sound? That is, is hydrocarbon emission control an optimum approach to urban oxidant reduction?"

It appears there is adequate reason to believe that in an urban situation the ambient level of oxidant is a function of the hydrocarbon emissions that occur from relatively nearby locations. There is also a great deal of evidence that oxidants from natural causes are significant; in fact, some claim (with seemingly good reason) that the air quality standards in certain areas may not be achievable because of naturally occurring oxidants. However, in most urban situations, it appears logical to conclude that, whatever the level of naturally occurring oxidants may be, local emissions of hydrocarbons are at least partially responsible for the local oxidant situation. It certainly is nowhere suggested that reduction in hydrocarbons can have anything but a beneficial effect in terms of reducing oxidants — the only disagreement being to what extent oxidants can be improved.

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The second questions asks: "Insofar as the urban oxidant problem is concerned, is NO_x emission control imperative? desirable? tolerable? undesirable? intolerable?"

The issue paper notes that "NO_x control has varying effects depending on the hydrocarbon to NO_x ratio of the reacting emissions." This statement appears adequately supported by the data in the various papers given at the International Conference and would seem to give rise to the argument that, in at least some situations, NO_x should not be controlled since it may result in less scavenging of oxidants and, therefore, higher observed ambient concentrations. In fact, I suppose that argument could be expanded to promote the introduction of additional NO_x into an urban area to scavenge oxidants.

It appears amply demonstrated that, in addition to hydrocarbons, NO_x emissions are a substantial cause of observed ambient concentrations of photochemical oxidants. Although there may be theoretical arguments that some would make to defend against controlling NO_x, it appears much more reasonable to conclude that control of NO_x emissions should improve the oxidant situation as looked at from a broader perspective than just the immediate urban environment where the NO_x emission is occurring. There appears good reason to believe that the control of the rural oxidant problem will only be achieved through control of NO_x emissions that occur, not only in the rural environment, but also in the urban environment. Therefore, if it is necessary to select one of the suggested answers to the basic question, I would select "desirable."

The issue paper then addressed four approaches at defining the source-receptor relationship between oxidants and emissions. Without discussing the relative merits of any one of these four approaches, or for that matter, suggesting any other approach, it would appear to me that with all of the disagreement, uncertainties, and confusion surrounding this issue, that the optimum control strategy should be developed based on the qualitative aspects of the source-receptor relationship rather than the quantitative aspects. If so, given the answer to the first question, maximum reasonable control of hydrocarbon emissions seems indicated.

It appears that nearly all investigators have at this moment rejected Appendix J. The heir apparent to the accepted method appears to be the isopleth method posed by Dimitriades; however, there is sufficient controversy surrounding that approach not to use it without further documentation.

In my opinion, the current Clean Air Act requires the impossible to be done. The country will not attain the ambient air quality standard for photochemical oxidants by mid-1977, and there is absolutely nothing EPA nor anyone else can do to cause it to happen. It is time to tell that to Congress.

It would not be a service to the Congress nor to the American public to pretend to develop control strategies which will achieve the standards because of some fictitious new method of describing quantitatively the source-receptor relationship. Let's be honest with everyone, including ourselves, and admit that we are dealing with a very difficult problem, that we are going to continue to attempt to develop the relationship (assuming we ever have the intelligence to do so), but meanwhile make every reasonable effort to control those things we have good cause to believe are involved in the problem and which we have the national will to control.

The first step in a control strategy should be to obtain relief from the Congress in amendments to the Clean Air Act to remove the imperatives of meeting this standard in a specified time. The Clean Air Act could, perhaps, even be so drastically amended as to reflect the fact that we may be dealing with such complex relationships that mortal man does not know the answer. In fact, man may not even be causing some of the problems. Since the majority of the scientific community appears willing to accept the fact that reducing hydrocarbons is a positive step in oxidant control, let us then begin with applying reasonably available control technology to significant existing hydrocarbon sources. This can be done in a couple different ways. One way is to rely upon the States to do it; however, because of the transport nature of the precursor compounds and of oxidants themselves, it is quite likely that the states in which the problems exist do not have control over the sources of contaminants causing the problem. Certainly States should be encouraged to address those aspects of the problem that they are capable of addressing. EPA

guidance and encouragement in this area are important. The current Federal plan to develop Reasonably Available Control Technology (RACT) documents to give the States guidance as to what type of controls are available for certain industrial processes will provide many States with the basis for getting into the business of controlling hydrocarbon sources. There are those, however, that will not.

If meaningful progress is to be made, EPA must develop a national plan to deal with hydrocarbon emissions. The first step should be the development of new source performance standards dealing with all significant stationary hydrocarbon sources. EPA may also wish to look at Section III(d) of the Clean Air Act to require States to then adopt controls for existing hydrocarbon sources (it appears to me that hydrocarbons meet the definiton of a "designated pollutant").

When EPA feels it has justification to define regional problems, EPA has the authority to develop regional plans and promulgate regulations affecting sources within those regions.

EPA should develop a national strategy for transportation controls. Many of the controls that have been suggested are highly socially disruptive; also, many come with incredibly high price tags. Components of transportation control strategies that are "reasonable" should be determined at the Federal level, preferably by act of Congress. It is not realistic to expect a State to enact stringent controls affecting its citizens when the benefits to be derived from those controls are practically impossible to quantify and may not even be realized within that State. If EPA is correct about the transboundary nature of the problem (and there appears ample reason to believe that they are), the national policy should not be to deal with the problem on a State-by-State basis.

In summary, I believe the following would be a reasonable approach to an oxidant control strategy until a more rational determination can be made of the source-receptor relationship of hydrocarbons, NO_x, and oxidants:

- Reasonably available control technology for stationary sources should be defined by the Federal Government and should be implemented by those States required to do so because of State Implementation Plan (SIP) deficiencies. EPA should promulgate RACT regulations for those areas with SIP deficiencies, if the States fail to do so.

- In States where EPA has not determined SIP deficiencies, EPA should encourage the States to implement RACT requirements when it is reasonable to conclude that emissions from sources in that State result in problems outside of the State.

- Where the need for regional (multistate) plans can be documented, EPA should promulgate such plans with the cooperation of the affected States. This is especially true where large metropolitan areas are upwind of nonattainment areas, but are not themselves in a nonattainment area.

- EPA should expedite the promulgation of new source performance standards for all significant stationary sources of hydrocarbons and NO_x.

- EPA should investigate the applicability of Section III(d) to hydrocarbon emissions.

- A national policy should be developed on transportation control strategies. This national policy should consist of a decision, by Congress, on mandatory components of an approvable Transportation Control Plan (TCP). Any additional restraints should be left to State option.

- The present effort to develop a cause/effect relationship of emissions and ambient levels of oxidants should be continued and, in fact, increased. However, excessive control programs should not be demanded at this time because of the amount of hydrocarbon control predicted as necessary by Appendix J or by any of the alternatives yet proposed.

REVIEW AND ANALYSIS

George T. Wolff

INTRODUCTION

Since 1971, when the U.S. EPA formulated and legislated into use the first oxidant control strategy, it has come under sharp criticism from State air pollution officials, scientific and university groups. The primary reasons for these criticisms were: a definitive quantitative relationship between hydrocarbons and oxidants was not established, the role of nitrogen oxides was not included, transport was not considered, and nonanthropogenic contributions were ignored.

As a result of these questions, the U.S. EPA, State agencies, industry, and research institutions undertook extensive research activities within the past 4 years to reexamine the entire oxidant control problem. The purpose of this report is to: review these recent studies that have dealt with determining oxidant-precursor relationships, and attempt to define an optimum control strategy for oxidants.

The questions that have been addressed are listed below.

- Are anthropogenic precursor controls even warranted?
- Is a hydrocarbon control strategy by itself sufficient to reduce oxidants?
- Do we also need to apply emission controls on sources that produce oxides of nitrogen?
- In terms of a cause-effect relationship, which cause (source) do we control: local, upwind, or both?

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- In terms of a cause-effect relationship, which effect do we design our strategy to eliminate: the local net oxidant production, the upwind or fossil oxidant, or both?

THE CASE FOR ANTHROPOGENIC PRECURSOR CONTROLS

The oxidant problem in the Eastern United States is associated during the summertime with high pressure systems which typically originate in Central Canada, move southeastward over the Midwestern States, and then eastward to the Atlantic Ocean. Data gathered for the entire 1976 oxidant season by the "Moodus Data Analysis Task Force" (53) indicate that oxidant (ozone) concentrations within these high pressure systems, as they first come out of Canada, are generally between 30-50 ppb. By the time the high has moved off the Atlantic coast and the Northeastern States, which are on the backside of the high, levels approaching 300 ppb are observed.

The increase in the ozone is undoubtedly due to a combination of ozone synthesis from both anthropogenic and natural precursors as well as stratospheric injection. An examination of ozone isopleth maps covering the 20-state Moodus study area on the initial days of an ozone episode (initial day is defined as the first day the Canadian high is located in the United States and contains ozone levels exceeding the NAAQS) indicate that anthropogenic precursor emissions are the principal cause of the elevated ozone. According to the U.S. EPA's hydrocarbon emission inventory map (Figure 1), two areas with extremely high hydrocarbon emission densities can be discerned in the central and eastern Midwestern States and in the Washington, D. C., to Boston, Mass., corridor. Figures 2 and 3 show typical initial days of an ozone episode. It is quite obvious that the areas of elevated ozone originated in the two high-density emission areas. As the high persists over the United States for several days, the ozone area in the Midwest generally builds eastward until the two areas merge. Figures 4 and 5 show typical days after the merging has taken place. The relationship between the areas of the high ozone and the high-emission density areas is still evident though.

Recently, Hathorn and Walker (18) proposed that the source of the additional ozone required to cause an episode in the backside of a high is stratospheric.

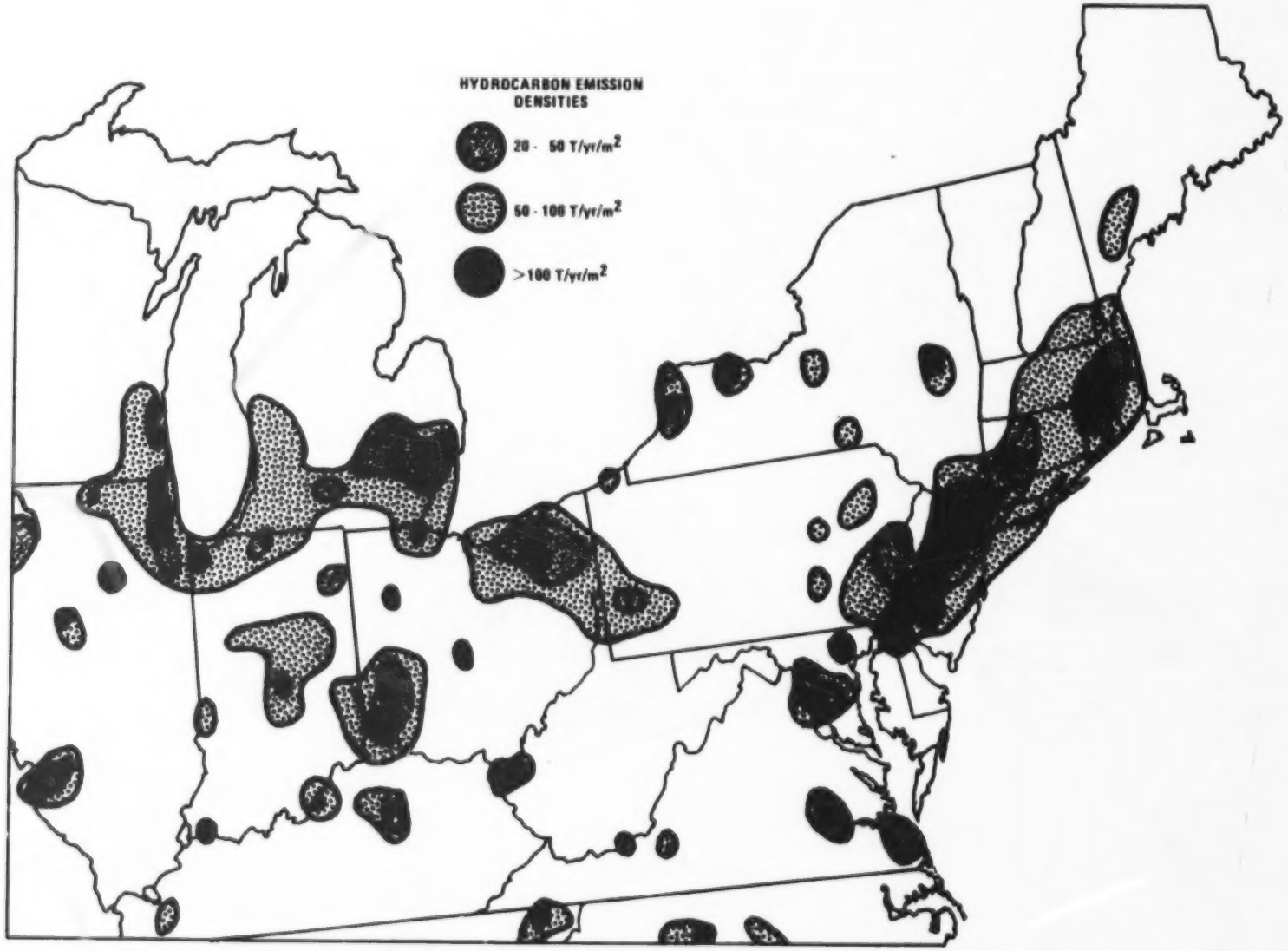

Figure 1. Hydrocarbon emissions.

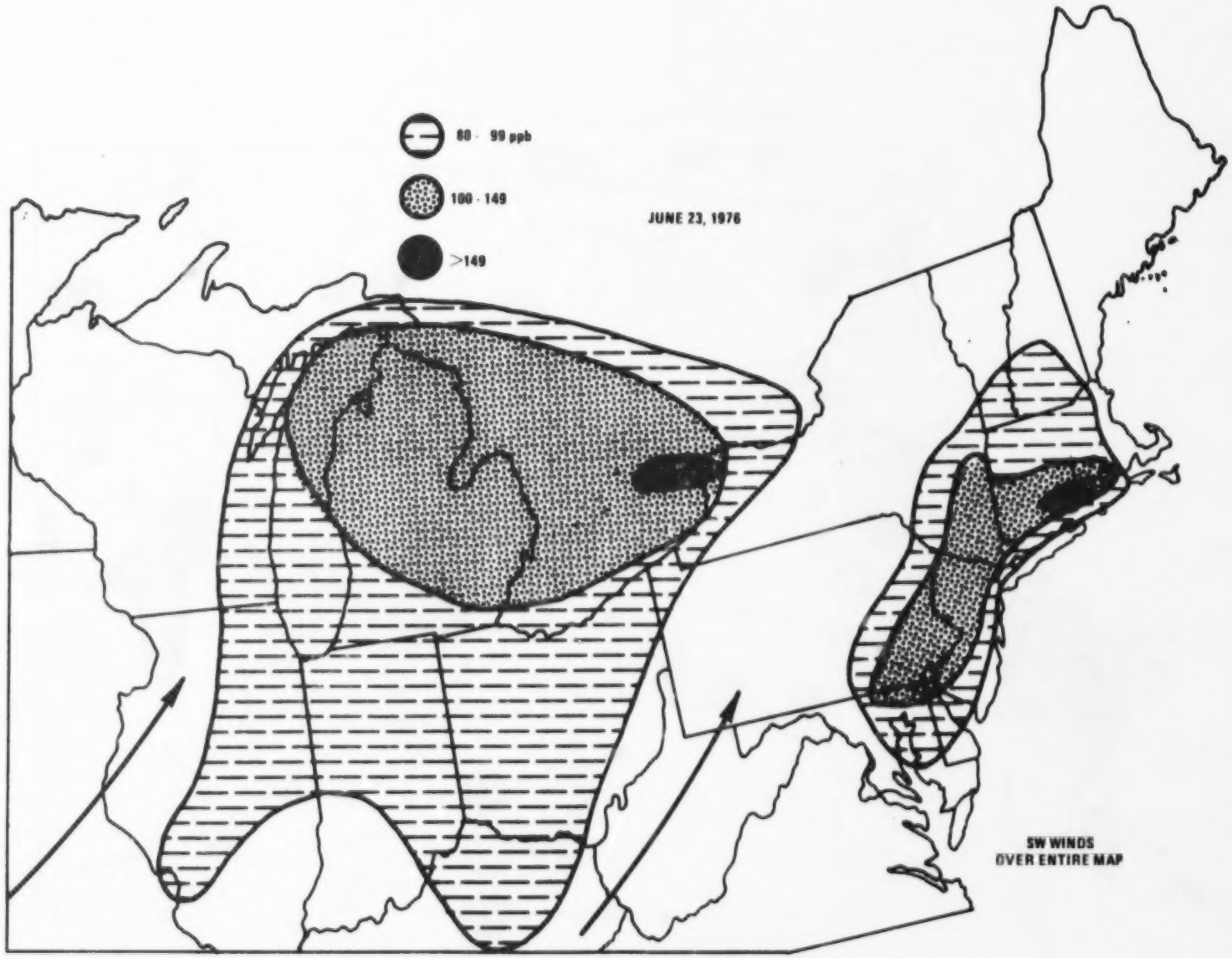

Figure 2. Surface ozone distribution.

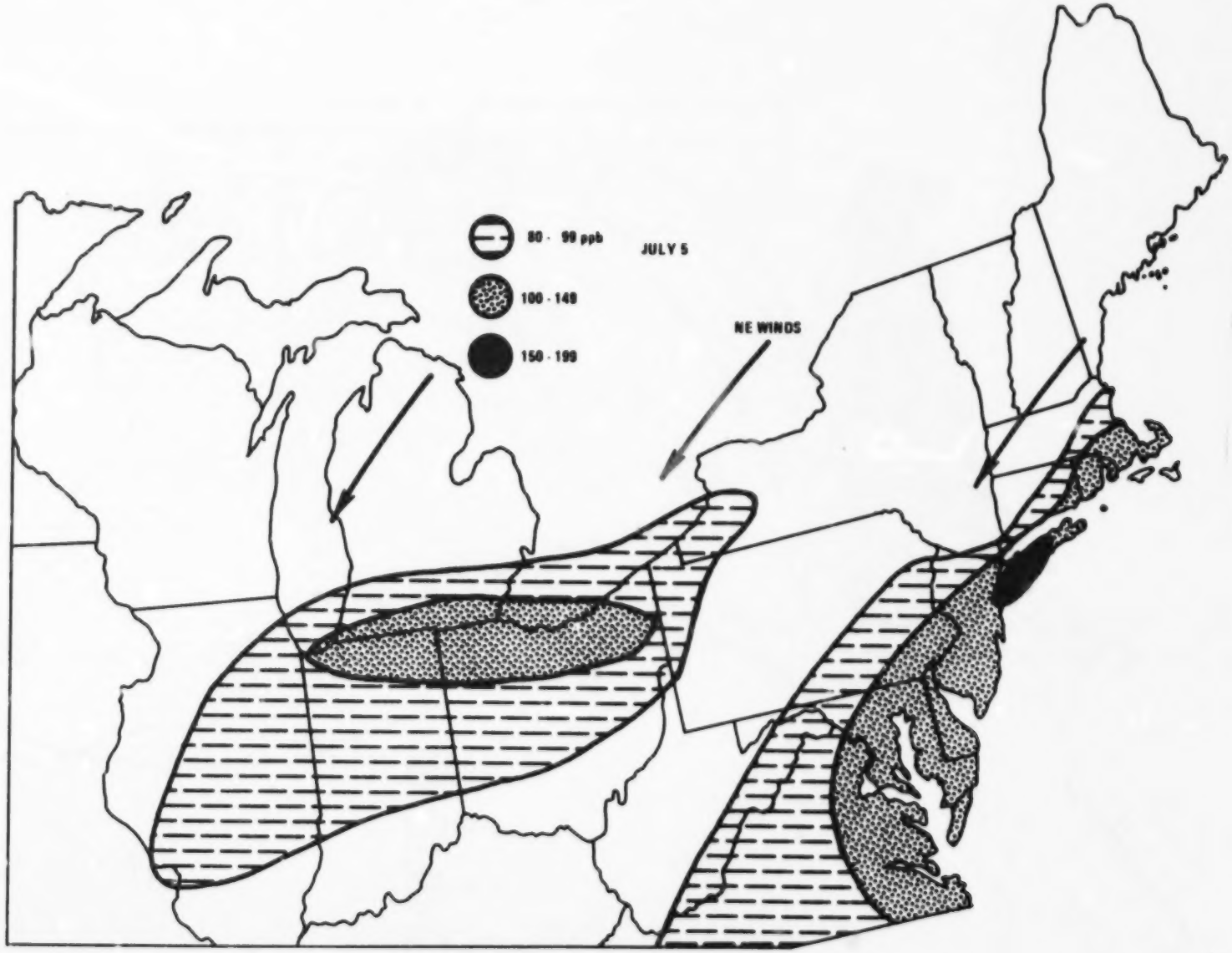

Figure 3. Surface ozone distributions.

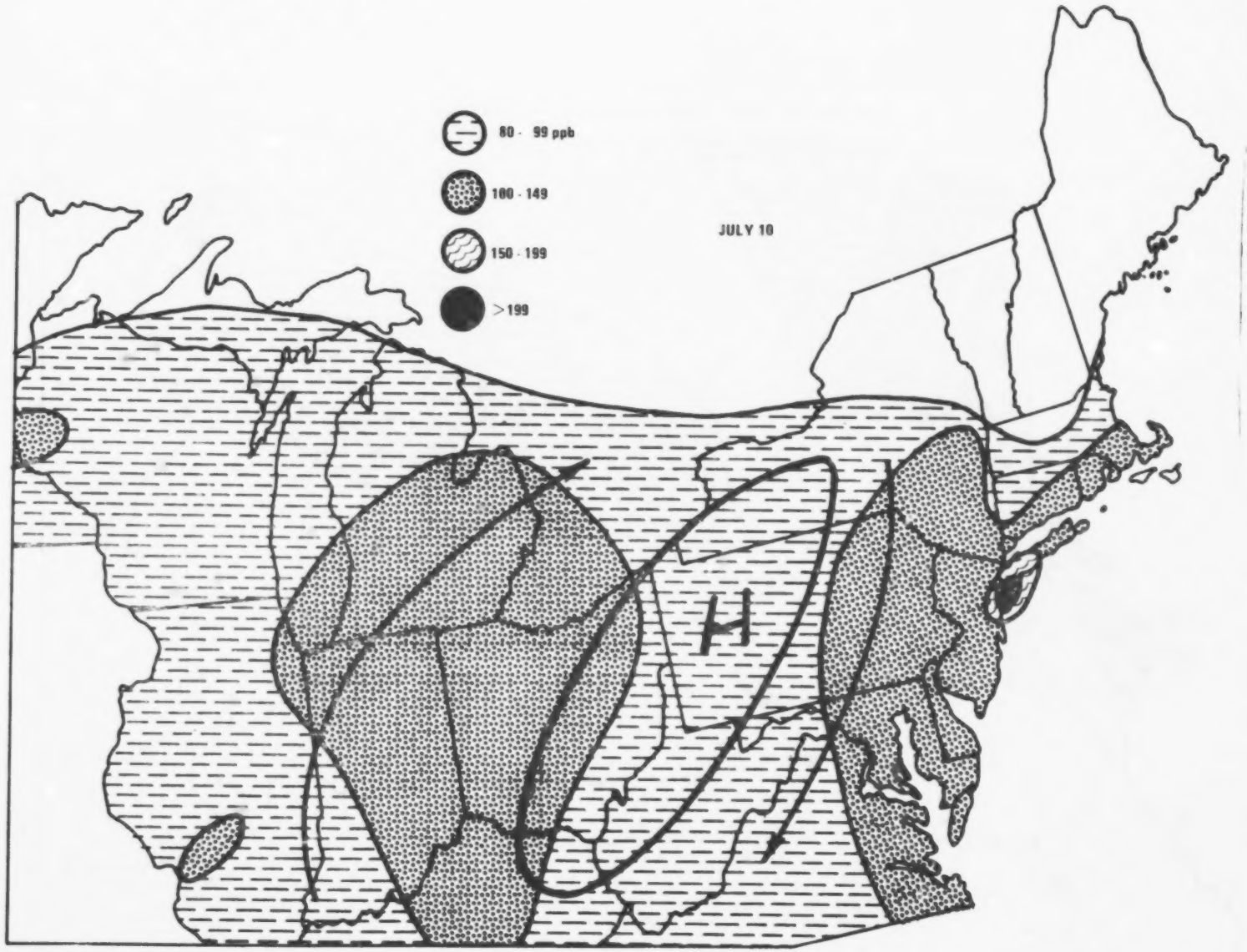

Figure 4. Surface ozone distributions.

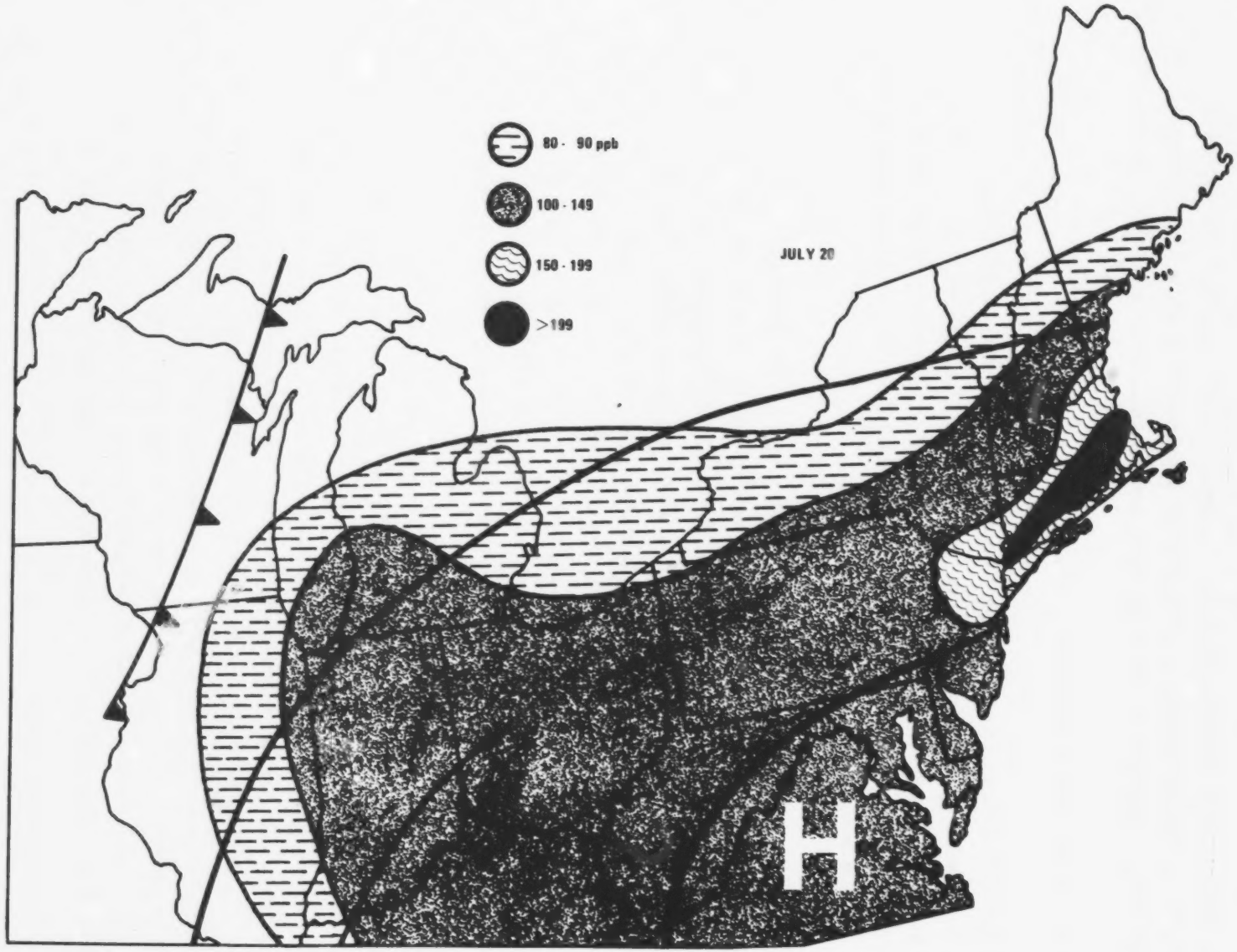

Figure 5. Surface ozone distributions.

The Moodus data, which does not discount a stratospheric contribution, indicate that man-made pollution sources are capable of providing the additional ozone associated with an episode in the Midwestern and Northeastern United States.

THE CASE FOR NONMETHANE HYDROCARBON CONTROLS

The most significant supporting evidence for a hydrocarbon reduction strategy as a means of reducing oxidants was shown by Dimitriades (49,54) and is based largely on the chamber studies and mathematical simulations of Dodge (10). From these studies, a series of ozone isopleths as a function of initial NMHC and NO_x has been developed.

Supporting evidence has been presented by a number of investigators. Meyer et al. (20) found a significant correlation between locally emitted hydrocarbons and afternoon ozone values at urban sites and between the previous morning's hydrocarbon emissions and afternoon's ozone at nonurban and rural sites. Using a numerical photochemical simulation model, Dabberdt and Singh (13) concluded that a reduction in hydrocarbons on the first day of an oxidant episode in the South Coast Air Basin would result in lower peak oxidant values. Data presented by Decker et al. (30) and Wolff et al. (55) have shown evidence of significant oxidant production downwind of petroleum refineries.

Ambient oxidant trends have also been compared with hydrocarbon emission trends. In both the South Coast Air Basin (Metropolitan Los Angeles) and the Bay Area Air Basin (Metropolitan San Francisco), substantial reductions in hydrocarbon emissions have been achieved since 1964. In the South Coast Basin where hydrocarbon emissions decreased 18% from 1964-1974, Trijonis et al. (15) found that the basinwide oxidants decreased 19% over the same period. Similarly, Martinez et al. (16) found significant reductions in the second highest annual ozone maximum, the average ozone maximum, the third-quarter average maximum, and the frequency of emissions greater than 0.08 ppm at most sites in the Bay Area Basin where hydrocarbon emissions were reduced 24% from 1964 to 1974.

The evidence presented by Dimitriades (49,54), Dodge (10), Meyer et al. (20), Dabberdt and Singh (13), Decker et al. (30), and Wolff et al. (55) indicate the need for hydrocarbon controls. Although the trend analysis conducted by Trijonis et al. (15) and Martinez et al. (16) indicates decreasing oxidant levels with decreasing hydrocarbon emissions, the results are far from conclusive because, during the same period (1964-1974), NO_x emissions increased in the South Coast Air Basin by 36% and in the Bay Area Air Basin by 31%. The possible effects of these increases are discussed in the next section.

THE CASE FOR NO_x CONTROLS

While most investigators are in agreement concerning the need for non-methane hydrocarbon controls, they are divided on the need for NO_x controls. The conflicting views have been attributed by Dimitriades (54,56) to the dual role of nitrogen oxides in the photochemical smog complex. At high ratios of NMHC/NO_x (<8-10), the addition of NO_x increases the maximum observed O_3 in the chamber studies. At low NMHC/NO_x ratios (<8-10), an increase in the NO_x will lower the maximum observed ozone. This is a result of the rapid $NO + O_3 \rightarrow NO_2 + O_2$ reaction, which becomes extremely important at these low ratios. As a result, Dimitriades (56) predicts that a reduction in urban NO_x levels will increase urban ozone, some of which may be transported into downwind areas and hence increase the downwind or rural oxidant burden. Dabberdt and Singh (13), on the other hand, feel that any emission reductions, both NO_x and NMHC, may result in a decrease in the total oxidant formation potential that may not be realized for several days after the reductions have been initiated.

The evidence against NO_x controls (above those necessary to achieve the NAAQS for NO_2) are summarized.

Meyer et al. (20) found a negative correlation between locally emitted NO_x emissions and maximum O_3 levels in urban areas. The classical case of decreasing NO_x levels resulting in increasing ozone levels in urban areas is the "Sunday Effect" reported by Cleveland et al. (14) and modeled by Farrow et al. (57). At several highly urbanized sites in northeastern New Jersey,

Cleveland et al. (14) observed that on Sundays, when ambient levels of NO were significantly lower than on weekdays, the ozone values tended to be slightly higher. This system was successfully modeled by Farrow et al. (57), who attributed it to the higher rate of O_3 scavenging by NO and NO_2 on weekdays. In their analysis of an air pollution episode in Los Angeles, Dabberdt and Singh's model (13) predicted a significant increase in ozone downwind of a power plant, if NO_x emission controls were used by the power plant.

The preceding discussion indicates that NO_x controls will result in an increase in the ozone levels in many urban areas. An exception to this was presented by Walker (41) who examined data from urban sites in Texas. His analysis indicates that the highest ozone values are observed in Texas when the early morning NMHC are between 5-10 ppm. At values above and below this, lower ozone maximums were observed. This suggests that NO_x may be the controlling parameter in Texas. He also states that NMHC/NO_x ratios in Texas average from 17.5/1 to 70/1. With these ratios, according to the O_3-NMHC-NO_x relationships developed by Dodge (10) and Dimitriades (54), NO_x controls would be the most effective approach.

The most important evidence for the use of NO_x controls appears in the data presented by Dimitriades (54) and Dodge (10). As mentioned above, it is apparent from their data that maximum ozone is obtained at a NMHC/NO_x ratio between 8/1 and 10/1. This is also the transition point where the role reversal of NO_x occurs. At ratio's greater than 8/1-10/1, the effect of NO_x reductions on ozone reductions become greater than a proportional reduction in NMHC reductions. In a recent report (52), EPA summarizes ambient NMHC/NO_x ratios obtained by various contractors. (This is shown in Table 1.) Of the 10 urban sites where these measurements have been made, 8 out of 10 have ratios greater than or equal to 8/1. Ten out of 10 suburban sites and 6 out of 6 rural sites also have ratios greater than 8/1. As a result, most of the sites would experience a greater ozone reduction if NO_x controls were employed. For those sites close to 8/1, the maximum benefit would be achieved with both NO_x and HC controls. The same EPA report (52) shows the NMHC/NO_x-O_3 relationships obtained from chamber studies using "aged precursors." These studies indicate

TABLE 1. AMBIENT NMHC, NO_x, AND NMHC/NO_x LEVELS AT SELECTED MONITORING SITES

(1)	(2)	(3)	(4)	(5)	(6)
Location	Type of Site	Distance to Nearest Population Center > 50,000 Miles	6-9 a. m. Mean NMHC/NO_x ppmC/ppm	6-9 a.m. Median NMHC/NO_x Ratio	Sampling Period (Days)
Austin, Tx.	Urban		.28/.025	10.6:1	7/1-9/30/75 (43 days)
Corpus Christi, Tx.	Urban		.65/.035	18.5:1	7/1-9/30/75 (44 days)
Dallas, Tx.	Urban		.13/.038	5.0:1	7/1-9/30/75 (44 days)
Los Angeles, Ca.	Urban		1.47/.147	9.8:1	7/1-9/30/75 (58 days)
Canton, Oh.	Urban		.99/.090	9.0:1	7/1-7/25/74 (14 days)
San Antonio, Tx.	Urban		.21/.022	11.2:1	7/1-9/30/75 (37 days)
El Paso, Tx.	Urban		.56/.064	9.2:1	7/1-9/30/75 (42 days)
St. Louis, Mo.	Urban			8.0:1Δ	July-Oct'75/June-Oct'76
Houston, Tx.	Urban		1.14/.135	7.7:1	7/1-9/30/75 (43 days)
Phoenix, Az.	Urban		2.04/.110	21.9:1	9/24-10/1/73 (7 days)
Azusa, Ca.	Surburban	20 mi ENE of LA CBD	1.23/.146	8.5:1	7/1-9/30/75 (86 days)
Canton, Oh.	Surburban	2 mi N of Downtown	.65/.073	9.4:1	7/1-7/24/74 (17 days)
Aldine, Tx.	Surburban	12 mi NNE of Houston	.53/.050	10.0:1	7/1-9/30/75 (21 days)
Clute, Tx.	Surburban	40 mi S of Houston	.53/.025	22.5:1	7/1-9/30/75 (49 days)
El Paso, Tx.	Surburban	5 mi ESE of Downtown	.48/.027	11.5:1	7/1-9/30/75 (30 days)
Texas City, Tx.	Surburban	10 mi NW of Galveston	.91/.017	40.0:1	7/1-9/30/75 (23 days)
Nederland, Tx.	Surburban	7 mi NW of Port Arthur	.66/.034	21.7:1	7/1-9/30/75 (36 days)
West Orange, Tx.	Surburban	20 mi E of Beaumont	.35/.023	18.0:1	7/1-9/30/75 (44 days)
Groton, Ct.	Surburban	2 mi S of New London-Groton, 40 mi ENE of New Haven	.24/.029	9.5:1	7/15-8/21/75 (15 days)
Portland, Me.	Surburban	2 mi NW of Downtown	.32/.034	11.4:1+	7/29-8/27/75 (5 days)
Lawrenceville, Ill.	Rural	∿ 50 mi N of Evansville, Ind. 2 mi ENE of Large Refinery	.22/.024	8.6:1	6/13-6/23/74 (10 days)
Pownal, Me.	Rural	∿ 17 mi NE of Portland, Me.	.42/.005	95.0:1	7/29-8/27/75 (22 days)
Simsburgy, Ct.	Rural	10 mi NW of Hartford, Ct.	.44/.006	47.0:1	7/15-8/22/75 (14 days)
McConnelsville, Oh.	Rural	63 mi SE of Columbus, Oh.	.30/.006	54.0:1*	6/14-8/31/74
Wilmington, Oh.	Rural	27 mi E of Dayton, 40 mi NE of Cincinnati, Oh.	.12/.007	17.5:1*	6/14-8/31/74
Wooster, Oh.	Rural	30 mi W of Akron and Canton, Oh.	.33/.008	40.0:1*	6/14-8/31/74

* Mean rather than median ratios

\+ On days when the site was downwind from Portland. When the site was upwind, the median ratio was 31:1.

Δ Mean median value for 2 summer's data at 6 sites in the City of St. Louis

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that the critical ratio for NO_x controls to be proportionately more effective than NMHC controls is as high as 30/1.

Additional support for NO_x controls have been presented by Meyer et al. (20), Van Ham and Niebor (21), Farrow et al. (57) and Wight (unpublished data).

In their empirical correlation analysis, Meyer et al. (20) found a significant positive correlation between early morning upwind NO_x emissions on the *previous* day and afternoon ozone values at *rural* sites. Although a similar relationship was found with the previous day's hydrocarbon emissions, the extremely high NMHC/NO_x ratio observed at rural sites (>100/1) would preclude any benefit of implementing only NMHC controls in the upwind urban areas.

The experimental work of Van Ham and Niebor (21) also support the implementation of NO_x controls. Spiking ambient air samples collected in bags and exposing them to sunlight with NO_x, they found that increasing the NO_x not only increases the maximum ozone, but it also increases the time of irradiation required to reach the ozone maximum. Initially, the NO_x acts as an ozone scavenger, but at some point in time, which is a function of the NO_x concentration and the NMHC/NO_x ratio, the role of NO_x is reversed (as Dimitriades suggested). At this point, the NO_x, which is mostly NO_2 at this time, begins to become an increasingly effective supplier of the odd oxygen atom that is required for ozone production. In terms of the real atmosphere, increasing the NO_x concentration delays the formation of the ozone maximum (this explains why urban O_3 values decrease with increasing local NO_x emissions) but increases the ozone maximum, which may not be observed for many hours or many miles downwind. This is consistent with the observations of Meyer et al. (20) and the suggestion of Dabberdt and Singh (13) that reduction of all precursors will reduce the air pollution potential.

According to the model of Farrow et al. (57), the net increase in NO_x flux due to higher emissions on weekdays far outweigh the additional O_3 flux caused by decreased emissions on Sundays. If this is in fact true, the

"Sunday Effect" should not be observed at sites downwind of northeastern New Jersey. Unpublished data gathered by Wight using the same computational techniques of Cleveland et al. (14) show that Greenwich, Conn., does not experience a Sunday Effect (see Figure 6). In fact, the weekday values appear to be substantially higher.

There is some evidence that the zone of ozone depletion near large sources of NO_x emissions is quite limited, and ozone detectors located near such sources would differ widely from monitors located a few blocks away. Since most urban monitors are located in high density traffic areas (this is especially true in northeastern New Jersey where the "Sunday Effect" originated), they may only record a relatively small scale phenomenon. In 1974, Wolff et al. (58) obtained ozone measurements at 1,000 ft over several ozone monitoring sites and compared them with the surface levels in mid-afternoon. At 1,000 ft, there was no noticeable O_3 depression over the urban centers. In fact, the 1,000-ft ozone levels were extremely similar over most of northern New Jersey. At rural sites and at urban sites where the monitor was located away from a high traffic density area, there was extremely good agreement between the surface and 1,000-ft ozone measurements. Over the high traffic density area monitors, which incidentally were the sites used by Cleveland et al. (14) to demonstrate the "Sunday Effect," surface ozone values were between 40-50% of the ozone observed at the 1,000-ft level.

Additional evidence of the relatively small-scale impact of ozone depletion caused by local NO_x emissions was presented by Wolff (59). The New Jersey Department of Environmental Protection operated an ozone monitor on State Street in Trenton, New Jersey, during 1973 and 1974. In 1973, State Street was a heavily traveled vehicular thoroughfare. In early 1974, the street was blocked off to vehicular traffic and made into a pedestrian mall. There is no evidence that this decreased traffic in Trenton — it merely redistributed it to surrounding streets. Although no NO_x measurements were made, CO measurements, which should represent the relative NO changes, were made. Figure 7 shows that the average daily maximum CO values decreased 38%, while the average daily maximum ozone values increased 60%. This increase in ozone could not be explained by meteorological conditions since most New

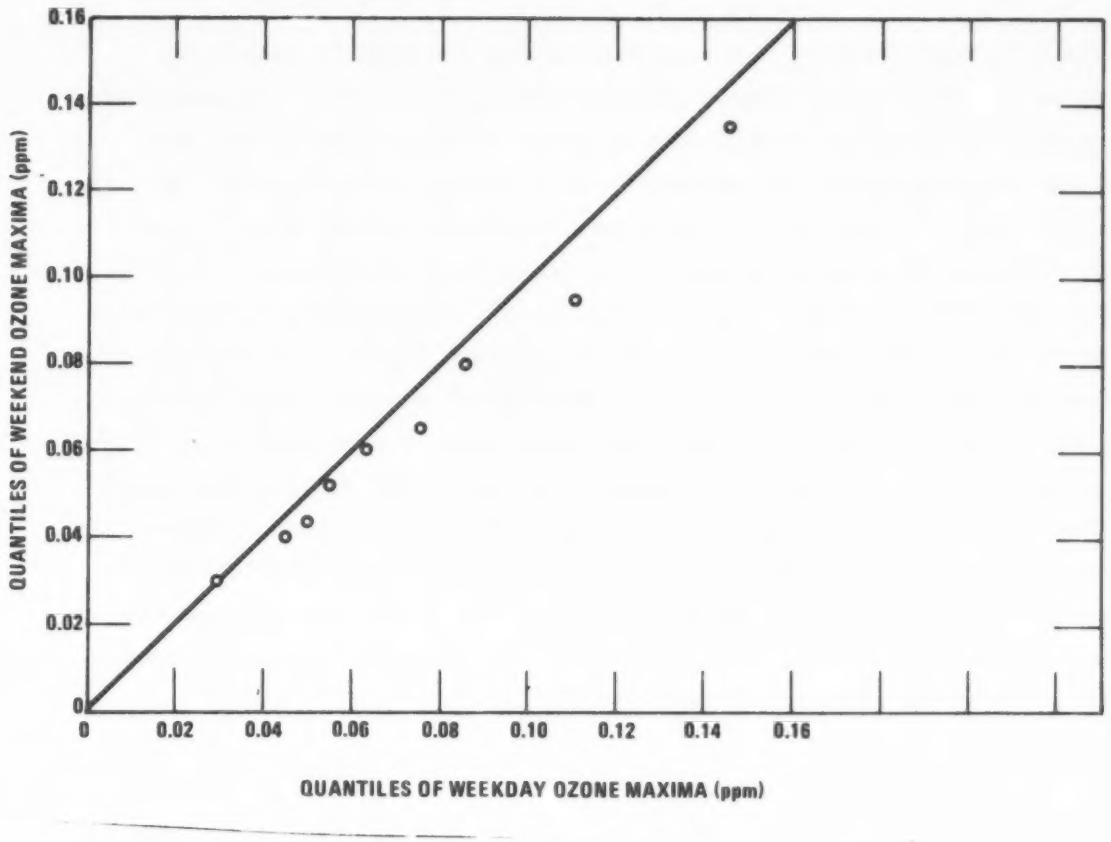

Figure 6. Greenwich, Conn. 1976, April-September ozone data Q-Q plot of maximum hourly values, weekends vs. weekdays.

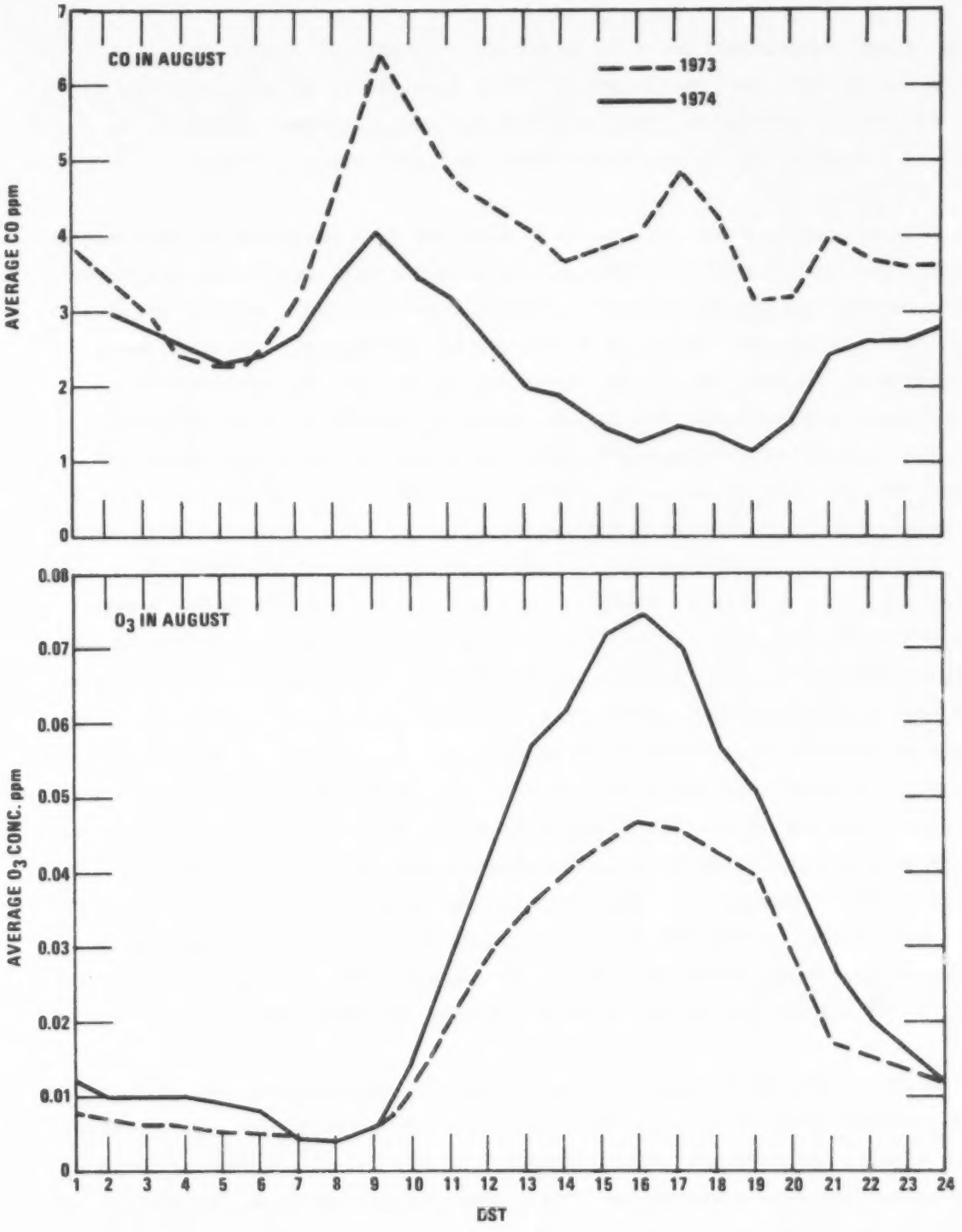

Figure 7. Trenton, New Jersey.

Jersey sites experienced lower O_3 in August 1974 than in August 1973. As a result, it is felt that the impact of ozone destruction by NO_x (role #1) is very limited in geographic scale and that the more important effect is to increase the ozone values short distances away from the NO_x sources.

As mentioned previously, the trend analyses data presented by Martinez et al. (16) and Trijonis et al. (15) are inconclusive with respect to the cause of the oxidant reductions in both the South Coast Air Basin and the Bay Area Air Basin. In the two areas, ozone reductions corresponded to hydrocarbon reductions of 18% and 24% and NO_x increases of 36% and 31%, respectively. According to the preceding discussion, these NO_x increases alone should be enough to account for the observed ozone decreases at the highly urbanized sites. To test this hypothesis, if the urban ozone reductions were due to NO_x increases, then according to the previous discussions, the ozone levels should have increased in downwind areas. On close examination of the data of Trijonis et al. (15), it is apparent that the sites which did record ozone reductions were confined to the densely populated counties of Los Angeles and Orange. The lesser densely populated counties of San Bernadino and Riverside, which are located downwind (to the east) of Los Angeles and Orange, do in fact report an average ozone increase of 8% over the same period (1964-1974). Similarly, a close examination of the data of Martinez et al. (16) indicates that the ozone reductions in the Bay Area Air Basin are generally confined to the eastern sections (the sites within and closest to San Francisco and Oakland), while increases in ozone levels have been observed at two out of the three easternmost (downwind) sites. Martinez et al. (16) also examined the trends at four other sites located in less densely populated areas of California. Three out of four sites showed an increasing ozone concentration trend.

Based on the discussions in this section, it is concluded that reductions in NO_x emissions in urban areas will increase the ozone values in a relatively small area in the proximity of and downwind of the reduced sources. These same reductions will decrease the total ozone-forming potential of the air and result in decreased ozone levels at downwind and rural sites. It has also been suggested by Farrow et al. (57) that a reduction in NO_x emissions will

reduce the organic and inorganic nitrates and reduce the potential of the atmosphere to cause lachrymation.

DEVELOPMENT OF A CAUSE AND EFFECT OXIDANT REDUCTION STRATEGY

It is widely accepted now that ozone is capable of being transported long distances (60). Urban plumes are distinguishable for nearly 100 miles downwind. Beyond this point, urban plumes merge and disperse, and this results in a relatively uniform ozone concentration extending for hundreds of miles within a particular air mass. During the day and at night above the nocturnal inversion layer, the ozone is somewhat conserved. Based on vertical ozone profile data, Sickles et al. (12) estimated the half-life to be 29.5 hr. Data from the DaVinci II experiment suggested a half-life between 16 and 34 hr. An extrapolation of Stasiuk and Coffey's (19) mean diurnal ozone profile at Whiteface Mt. yields a half-life of the order of 23 hr.

As a result of this relatively long half-life of ozone, local control strategies must deal not only with local emissions but also ozone transported into the area and the impact that the ozone produced by their local precursor emissions has on downwind cities. Transported ozone entering an urban area has been observed to be as high as 0.120 ppm in the Northeastern United States (61). Huffman et al. (43) observed ozone levels as high as 0.18 ppm being transported into a major Midwestern city. It appears that in the Eastern United States, high levels of ozone produced by one area's emissions are conserved and become some other downwind city's problem the next day. Consequently, control strategies must be designed to reduce the total ozone-forming potential.

An analogous situation exists in Southern California. In this case, however, the ozone is generally confined to the South Coast Air Basin because of its unique topographical features. The first day's spent emissions and generated ozone are conserved aloft, and these add to the second day's problem when the shallow nocturnal inversion is broken. Evidence supporting this has been presented by Dabberdt and Singh (13) and Johnson and Singh (62). Con-

sequently, control strategies in Southern California must also be designed to reduce the total ozone-forming potential.

Very limited data have been obtained to evaluate the effect of NMHC and NO_x concentrations on ozone production during multiday periods. As mentioned previously, Meyer et al. (20) found a positive relationship (significant at the 0.10 significance level) between rural O_3 levels and NO_x emissions 24 hours upwind. A weaker relationship was found for rural O_3 and NMHC emissions 30 hours upwind.

A few multiday smog chamber studies have been conducted, and they have been discussed by Dimitriades (56) and Sickles et al. (12). Although the data base is extremely limited, several observations relating to this discussion have been made.

In an attempt to simulate the real atmosphere, outdoor chambers were used. Sunlight was the only source of photons, and clean air was introduced at a constant rate to simulate atmospheric dispersion processes. The results clearly indicated that the dilution of ozone is not proportional to the dilution of the initial chamber air. The dilution of the ozone is substantially less (12,56). This supports the previously cited conclusion that at low NO_x concentrations, each NO_x molecule becomes more efficient in producing ozone (12).

A few multiday irradiations were conducted with different initial NMHC and NO_x concentrations. In one set of experiments, initial NMHC were depleted approximately 65%, while NO_x remained the same. During day 1, in the chamber with the reduced NMHC, ozone levels were reduced approximately 75%. On day 2, in the chamber with the uncontrolled NMHC, the ozone reached about the same maximum as it did on day 1. In the controlled chamber, ozone values nearly quadrupled from day 1 and reached a maximum of about 90% of ozone in the uncontrolled chamber. It appears that the effect of decreasing the NMHC and the $NMHC/NO_x$ ratio (from about 7.5 to 3) was to delay the formation of the ozone. Unfortunately, since this experiment ended on the second day, no conclusions

can be made concerning the effect of the NMHC reduction on the total ozone-forming potential.

Additional 3-day experiments conducted by Sickles et al. (12) with different initial precursor concentrations have indicated that there appears to be a general trend for lower ozone maximum of all 3 days when both initial NMHC and NO_x concentrations are reduced. In addition, day 2 and day 3 ozone maxima decrease with decreasing early morning NO_x and NMHC on subsequent days.

The data obtained in these multiday chamber studies appear to be consistent with the observations of Meyer et al. (20) using ambient data and with the data presented in the following subsection of this report. The most effective way of reducing ozone is to reduce both NMHC and NO_x. Unfortunately, the corresponding reduction in ozone will be substantially less than proportional.

Other chamber studies relating to oxidant control strategies were conducted by Jeffries et al. (9), who studied the effect of continuous emissions on oxidant precursor relationships. Two simultaneous experiments were conducted. In one chamber, all of the NMHC and NO_x were injected into the chamber at approximately 6 a.m. In the second chamber, the same total mass of precursors was added but ramp-injected over the 0600- to 1800-hr. period. The results showed that the ramp side usually forms O_3 faster and is higher in O_3 until the afternoon when the static side usually overtakes and slightly surpasses the ramped side. The total dosage of O_3 during the day in both chambers was nearly identical. This indicates that the 6 a.m.-9 a.m. emissions, which control strategies have been exclusively directed toward, are not the only emissions important in O_3 formation. On the contrary, the results indicate that controls should be applied to emissions throughout the day. In addition, this study indicates that the additive effect of nonurban emissions could be important and they should also be included in any control strategy.

SUMMARY AND CONCLUSIONS

Anthropogenic emissions of nonmethane hydrocarbons (NMHC) and nitrogen oxides (NO_x) are responsible for a substantial portion of the high oxidant (ozone) concentrations observed at both urban and rural locations in the United States.

Studies indicate that hydrocarbon reductions will result in greater oxidant reductions in urban than in rural areas. This is a result of a decrease in the NMHC/NO_x ratio, which would make NO_x a more effective O_3 scavenger in urban areas.

Reductions in NO_x in urban areas will result in local increases in ozone within the urban area, but the effect will be to reduce the ozone in downwind and rural areas.

It has been shown that ozone levels are generally lower on weekdays at sites with high weekday traffic densities. On Sundays with lower NO_x concentrations, the rate of ozone scavenging is reduced, and consequently the measured ozone is higher. Downwind on Sundays, however, lower ozone levels are observed.

Because of long-range transport, it is not enough for any urban area to develop a control strategy designed to achieve the NAAQS for oxidants in their area without any concern for those areas downwind. Controls must be placed on upwind sources to assure that the upwind source area meets the NAAQS and to allow the downwind areas to meet the NAAQS by applying their own reasonable local controls. Multiday chamber studies to date have not provided any quantitative evidence demonstrating the degree of control required for this approach. It is evident, however, that severe reductions of both NO_x and NMHC are required. Consequently, until such quantitative information is available, the most feasible short-term approach appears to be a modification of that adopted by the "Moodus" States (63). Their approach is to control hydrocarbons with the best available control technology which incorporates advances

in the state of the art. The required modification is to extend the "Moodus" approach to include the control of nitrogen oxides.

Finally, evidence has been presented that indicates that the control of only 6 a.m.-9 a.m. precursor emissions is inadequate. Instead, control of all emissions throughout the day is needed. This applies to urban as well as nonurban sources.

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